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14. ABSTRACT
Our project on adaptive structural materials began with bone as a source of inspiration for adaptive materials systems. Examining the structure of natural bone leads to the five guiding principles for our research: (i) load bearing by hierarchically porous materials; (ii) adaptive, sensing load and supplying mass to reinforce at load-bearing sites through material deposition and dissolution; (iii) transport of materials using fluid flow through low density porous cy systems; (iv) energy to drive processes taken from storage sites, which are replenished by internal or external energy generation; (v) mechanisms, which are not fully understood for bone, but knowing the

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Report Title

INNOVATIVE DESIGN AND PROCESSING OF MULTI-FUNCTIONAL ADAPTIVE STRUCTURAL MATERIALS

ABSTRACT

Our project on adaptive structural materials began with bone as a source of inspiration for adaptive materials systems. Examining the structure of natural bone leads to the five guiding principles for our research: (i) load bearing by hierarchically porous materials; (ii) adaptive, sensing load and supplying mass to reinforce at load-bearing sites through material deposition and dissolution; (iii) transport of materials using fluid flow through low density porous cy systems; (iv) energy to drive processes taken from storage sites, which are replenished by internal or external energy generation; (v) mechanisms, which are not fully understood for bone, but knowing the fundamental mechanisms allows these to be adjusted for application to synthetic systems. The problem as defined in the third year of the program was how to change soft materials into hard structures reversibly, in response to load or other environmental stresses. The approaches we used in the third year of the program include (i) reversible jamming, layering, welding and/or percolation; (ii) dissipative materials; and (iii) granular chemistry.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper
01/09/2014 48.00	Shengqiang Cai, Dayong Chen, Zhigang Suo, Ryan C. Hayward. Creasing instability of elastomer films, Soft Matter, (08 2012): 1301. doi: 10.1039/c2sm06844c
01/09/2014 46.00	Lloyd Han, Lihua Jin, Zhigang Suo, David A. Weitz, Adam R. Abate. Measuring the elastic modulus of microgels using microdrops, Soft Matter, (08 2012): 10032. doi: 10.1039/c2sm26108a
01/09/2014 47.00	Christian Punckt, Michael Bozlar, Sibel Korkut, Jian Zhu, Choon Chiang Foo, Zhigang Suo, Ilhan A. Aksay. Dielectric elastomer actuators with elastomeric electrodes, Applied Physics Letters, (08 2012): 91907. doi: 10.1063/1.4748114
01/09/2014 49.00	Wonjae Choi, Michinao Hashimoto, Audrey K. Ellerbee, Xin Chen, Kyle J. M. Bishop, Piotr Garstecki, Howard A. Stone, George M. Whitesides. Bubbles navigating through networks of microchannels, Lab on a Chip, (10 2011): 0. doi: 10.1039/c1lc20444k
01/09/2014 50.00	Dan Du, Zhexiang Zou, Yongsoon Shin, Jun Wang, Hong Wu, Mark H. Engelhard, Jun Liu, Ilhan A. Aksay, Yuehe Lin. Sensitive Immunosensor for Cancer Biomarker Based on Dual Signal Amplification Strategy of Graphene Sheets and Multienzyme Functionalized Carbon Nanospheres, Analytical Chemistry, (04 2010): 2989. doi: 10.1021/ac100036p
01/09/2014 51.00	Douglas P. Holmes, Behrouz Tavakol, Guillaume Froehlicher, Howard A. Stone. Control and manipulation of microfluidic flow via elastic deformations, Soft Matter, (05 2013): 7049. doi: 10.1039/c3sm51002f
01/09/2014 52.00	Sung Hoon Kang, Sicong Shan, Wim L. Noorduin, Mughees Khan, Joanna Aizenberg, Katia Bertoldi. Buckling-Induced Reversible Symmetry Breaking and Amplification of Chirality Using Supported Cellular Structures, Advanced Materials, (06 2013): 3380. doi: 10.1002/adma.201300617
01/09/2014 53.00	Tiefeng Li, Christoph Keplinger, Richard Baumgartner, Siegfried Bauer, Wei Yang, Zhigang Suo. Giant voltage-induced deformation in dielectric elastomers near the verge of snap-through instability, Journal of the Mechanics and Physics of Solids, (02 2013): 611. doi: 10.1016/j.jmps.2012.09.006
01/09/2014 54.00	C. Keplinger, J.-Y. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides, Z. Suo. Stretchable, Transparent, Ionic Conductors, Science, (08 2013): 984. doi: 10.1126/science.1240228
01/09/2014 55.00	Tong-Qing Lu, Zhi-Gang Suo. Large conversion of energy in dielectric elastomers by electromechanical phase transition, Acta Mechanica Sinica, (09 2012): 1106. doi: 10.1007/s10409-012-0091-x
01/09/2014 56.00	Ramses V. Martinez, Jamie L. Branch, Carina R. Fish, Lihua Jin, Robert F. Shepherd, Rui M. D. Nunes, Zhigang Suo, George M. Whitesides. Robotic Tentacles with Three-Dimensional Mobility Based on Flexible Elastomers, Advanced Materials, (01 2013): 205. doi: 10.1002/adma.201203002
01/09/2014 57.00	Yuyan Shao, Jun Wang, Hong Wu, Jun Liu, Ilhan?A. Aksay, Yuehe Lin. Graphene Based Electrochemical Sensors and Biosensors: A Review, Electroanalysis, (05 2010): 1027. doi: 10.1002/elan.200900571

01/09/2014 58.00 Jeong-Yun Sun, Xuanhe Zhao, Widusha R. K. Illeperuma, Ovijit Chaudhuri, Kyu Hwan Oh, David J. Mooney, Joost J. Vlassak, Zhigang Suo. Highly stretchable and tough hydrogels,
Nature, (09 2012): 133. doi: 10.1038/nature11409

01/09/2014 59.00 Zhiwen Tang, Hong Wu, John R. Cort, Garry W. Buchko, Youyu Zhang, Yuyan Shao, Ilhan A. Aksay, Jun Liu, Yuehe Lin. Constraint of DNA on Functionalized Graphene Improves its Biostability and Specificity,
Small, (06 2010): 1205. doi: 10.1002/smll.201000024

01/09/2014 60.00 Donghai Wang, Rong Kou, Daiwon Choi, Zhenguo Yang, Zimin Nie, Juan Li, Laxmikant V. Saraf, Dehong Hu, Jiguang Zhang, Gordon L. Graff, Jun Liu, Michael A. Pope, Ilhan A. Aksay. Ternary Self-Assembly of Ordered Metal Oxide?Graphene Nanocomposites for Electrochemical Energy Storage,
ACS Nano, (03 2010): 1587. doi: 10.1021/nn901819n

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International Journal of Solids and Structures, (03 2013): 920. doi: 10.1016/j.ijsolstr.2012.11.015

01/09/2014 62.00 Jian Zhu, Matthias Kollosche, Tongqing Lu, Guggi Kofod, Zhigang Suo. Two types of transitions to wrinkles in dielectric elastomers,
Soft Matter, (05 2012): 8840. doi: 10.1039/c2sm26034d

01/09/2014 63.00 J.C. Weaver, , G.W. Milliron, , P. Allen, , A. Miserez, , A. Rawal, , J. Garay, , P.J. Thurner, , J. Seto,, B. Mayzel, , L. Jon Friesen, , B.F. Chmelka, , P. Fratzl, , J. Aizenberg, , Y. Dauphin, , D. Kisailus,, D.E. Morse. Unifying Design Strategies in Demosponge and Hexactinellid Skeletal Systems,
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01/09/2014 65.00 Ilhan A. Aksay, Boris Khusid, Linda Jan, Christian Punckt. Directed Motion of Colloidal Particles in a Galvanic Microreactor,
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Soft Matter, (04 2010): 24210. doi: 10.1039/c000443j

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Acta Biomaterialia, (03 2010): 1001. doi: 10.1016/j.actbio.2009.09.002

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Journal of Materials Chemistry, (06 2010): 6009. doi: 10.1039/c0jm00696c

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Proceedings of the National Academy of Sciences, (05 2010): 10354. doi: 10.1073/pnas.1000954107

10/01/2012 16.00 Z. Suo, Y. Hu. Viscoelasticity and poroelasticity in elastomeric gels,
Acta Mechanica Solida Sinica, (10 2012): 0. doi:

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International Journal of Engineering Science, (12 2011): 1415. doi: 10.1016/j.ijengsci.2011.05.017

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Nano Letters, (11 2011): 0. doi: 10.1021/nl203332e

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MRS Bulletin, (03 2012): 0. doi: 10.1557/mrs.2012.32

10/01/2012 42.00 Joseph D. Roy-Mayhew, Gerrit Boschloo, Anders Hagfeldt, Ilhan A. Aksay. Functionalized Graphene Sheets as a Versatile Replacement for Platinum in Dye-Sensitized Solar Cells,
ACS Applied Materials & Interfaces, (05 2012): 0. doi: 10.1021/am300451b

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Journal of Applied Physics, (05 2012): 0. doi: 10.1063/1.4721777

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International Journal of Solids and Structures, (08 2012): 2187. doi: 10.1016/j.ijsolstr.2012.04.031

10/01/2012 38.00 Ramses V. Martinez, Carina R. Fish, Xin Chen, George M. Whitesides. Elastomeric Origami: Programmable Paper-Elastomer Composites as Pneumatic Actuators,
Advanced Functional Materials, (04 2012): 0. doi: 10.1002/adfm.201102978

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Physical Review E, (05 2012): 0. doi: 10.1103/PhysRevE.85.051801

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Soft Matter, (01 2010): 0. doi: 10.1039/b920392c

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Current Opinion in Solid State and Materials Science, (12 2011): 0. doi: 10.1016/j.cossms.2011.05.004

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Nature Protocols, (01 2012): 0. doi: 10.1038/nprot.2012.003

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Physical Review Letters, (09 2011): 0. doi: 10.1103/PhysRevLett.107.134503

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Nature Materials, (10 2011): 0. doi: 10.1038/nmat3144

10/01/2012 30.00 Christoph Keplinger, Tiefeng Li, Richard Baumgartner, Zhigang Suo, Siegfried Bauer. Harnessing snap-through instability in soft dielectrics to achieve giant voltage-triggered deformation,
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10/01/2012 26.00 Yuhang Hu, Jin-Oh You, Debra T. Auguste, Zhigang Suo, Joost J. Vlassak. Indentation: A simple, nondestructive method for characterizing the mechanical and transport properties of pH-sensitive hydrogels,
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10/01/2012 20.00 Lihua Jin, Shengqiang Cai, Zhigang Suo. Creases in soft tissues generated by growth,
EPL (Europhysics Letters), (09 2011): 0. doi: 10.1209/0295-5075/95/64002

10/01/2012 19.00 Huiming Wang, Shengqiang Cai, Federico Carpi, Zhigang Suo. Computational Model of Hydrostatically Coupled Dielectric Elastomer Actuators,
Journal of Applied Mechanics, (05 2012): 0. doi: 10.1115/1.4005885

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Journal of Applied Physics, (02 2012): 0. doi: 10.1063/1.3680878

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EPL (Europhysics Letters), (02 2012): 0. doi: 10.1209/0295-5075/97/34009

10/21/2011 2.00 Santiago Romero-Vargas Castrillo?n, Nicola?s Giovambattista, Ilhan A. Aksay, Pablo G. Debenedetti. Structure and Energetics of Thin Film Water,
The Journal of Physical Chemistry C, (03 2011): 4624. doi: 10.1021/jp1083967

10/21/2011 1.00 Shengqiang Cai, Katia Bertoldi, Huiming Wang, Zhigang Suo. Osmotic collapse of a void in an elastomer: breathing, buckling and creasing,
Soft Matter, (11 2010): 57700. doi: 10.1039/c0sm00451k

10/21/2011 3.00 Zhao H. Fang, Christian Punckt, Eva Y. Leung, Hannes C. Schniepp, Ilhan A. Aksay. Tuning of structural color using a dielectric actuator and multifunctional compliant electrodes,
Applied Optics, (12 2010): 6689. doi: 10.1364/AO.49.006689

10/21/2011 4.00 Douglas P. Holmes, Matthieu Roché, Tarun Sinha, Howard A. Stone. Bending and twisting of soft materials by non-homogenous swelling,
Soft Matter, (11 2011): 51880. doi: 10.1039/c0sm01492c

10/21/2011 5.00 Yuhang Hu, Xin Chen, George M. Whitesides, Joost J. Vlassak, Zhigang Suo. Indentation of polydimethylsiloxane submerged in organic solvents,
Journal of Materials Research, (1 2011): 785. doi: 10.1557/jmr.2010.35

10/21/2011 6.00 Pilnam Kim, Camille Duprat, Scott Tsai, Howard Stone. Selective Spreading and Jetting of Electrically Driven Dielectric Films,
Physical Review Letters, (7 2011): 0. doi: 10.1103/PhysRevLett.107.034502

10/21/2011 7.00 Philseok Kim, Alexander K Epstein, Mughees Khan, Lauren D. Zarzar, Darren J. Lipomi, George M. Whitesides, Joanna Aizenberg. Structural Transformation by Electrodeposition on Patterned Substrates (STEPS): A New Versatile Nanofabrication Method,
Nano Letters, (03 2011): 0. doi: 10.1021/nl200426g

10/21/2011 8.00 Sibel Korkut, Joseph D. Roy-Mayhew, Daniel M. Dabbs, David L. Milius, Ilhan A. Aksay. High Surface Area Tapes Produced with Functionalized Graphene,
ACS Nano, (06 2011): 52140. doi: 10.1021/nn2013723

10/21/2011 9.00 Shuyang Pan, Ilhan A. Aksay. Factors Controlling the Size of Graphene Oxide Sheets Produced,
ACS Nano, (05 2011): 4073. doi: 10.1021/nn200666r

10/21/2011 10.00 Christian Punckt, Michael A. Pope, Jun Liu, Yuehe Lin, Ilhan A. Aksay. Electrochemical Performance of Graphene as Effected by Electrode Porosity and Graphene Functionalization,
Electroanalysis, (12 2010): 2834. doi: 10.1002/elan.201000367

10/21/2011 11.00 Joseph D. Roy-Mayhew, David J. Bozym, Christian Punckt, Ilhan A. Aksay. Functionalized Graphene as a Catalytic Counter Electrode in Dye-Sensitized Solar Cells,
ACS Nano, (10 2010): 6203. doi: 10.1021/nn1016428

10/21/2011 12.00 Yuyan Shao, Sheng Zhang, Mark H. Engelhard, Guosheng Li, Guocheng Shao, Yong Wang, Jun Liu, Ilhan A. Aksay, Yuehe Lin. Nitrogen-doped graphene and its electrochemical applications,
Journal of Materials Chemistry, (09 2010): 7491. doi: 10.1039/c0jm00782j

10/21/2011 13.00 Liang Yan, Christian Punckt, Ilhan A. Aksay, Wolfgang Mertin, Gerd Bacher. Local Voltage Drop in a Single Functionalized Graphene Sheet Characterized by Kelvin Probe Force Microscopy,
Nano Letters, (09 2011): 3543. doi: 10.1021/nl201070c

10/21/2011 14.00 Bo Li , Liwu Liu, Zhigang Suo. Extension limit, polarization saturation, and snap-through instability of dielectric elastomers,
International Journal of Smart and Nano Materials, (03 2011): 59. doi:

10/21/2011 15.00 Zhigang Suo. Theory of dielectric elastomers,
Acta Mechanica Solida Sinica, (12 2010): 549. doi:

TOTAL: **68**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

J. Aizenberg

1. "Novel Self-Regulating Homeostatic Materials," M. Aizenberg, X. He, J. Aizenberg, Fron-tiers in Macromolecular and Supramolecular Science, Bucharest, Romania, June 7-14, 2013.
2. "Responsive, Self-regulated Systems: From Molecules to Devices," J. Aizenberg, Gordon Research Conference (GRC) on Self-Assembly & Supramolecular Chemistry, Les Diablerets, Switzerland, May 5-10, 2013.
3. "Slippery When Wet: Liquid-Infused Nanostructured Omni-Repellent Coatings and Biomed-ical Applications" P. Kim, New England Bioscience Society 2013 Annual Meeting, Harvard Medical School, Boston, MA, April 27, 2013.
4. "Rational Design of Omni-Repellent Liquid-Infused Nanostructured Surfaces and Their Manufacturable Coating Methods on a Wide Range of Materials," P. Kim, M. J. Kreder, J. Alvarenga, J. Aizenberg, Smart Coatings 2013, Orlando, FL, February 20, 2013.
5. 'Homeostatic Materials," M. Aizenberg, X. He, J. Aizenberg, Advanced Materials and Nano-technology (AMN)-6 Conference, Auckland, New Zealand, February 11-February 15, 2013. [Keynote speaker]
6. 'Everything SLIPS: Design of Novel Omniphobic Materials," J. Aizenberg, Advanced Mate-rials and Nanotechnology (AMN)-6 Conference, Auckland, New Zealand, February 11-February 15, 2013. [Keynote speaker]
7. "Slippery Materials that Repel Everything," J.Aizenberg, Materials Research Society Fall 2012 meeting, Boston, MA, November 27, 2012.
8. "Evaporation-Induced Self-Organization of Polymer Nanorod Arrays: When Structured Sol-ids Met a Liquid," S. H. Kang, B. Pokroy, N. Wu, L. Mahadevan, J. Aizenberg, 49th Society of Engineering Science Meeting, Atlanta, GA, October 2012.
9. "Liquid-Infused Nanostructured Surfaces with Extreme Anti-Ice and Anti-Frost Perfor-mance," P. Kim, T.-S. Wong, J. Alvarenga, M. J. Kreder, W. E. Adorno-Martinez, J. Aizen-berg, NIST/Industry Polymer Surface/Interface (PSI) Consortium, Wallingford, CT, October 2012.
10. "Autonomic Dynamic Materials Displaying Chemo-mechano-chemical Self-regulation," M. Aizenberg, X. He, O. Kuksenok, L. D. Zarzar, A. Shastri , A. C. Balazs, J. Aizenberg, Gel-sympo2012-Adaptive Hybrid Architectures Conference, Tsukuba, Ibaraki, Japan, October 9-11, 2012.
11. "Towards Dynamic Hybrid Architectures: Or Can We Make Materials Adaptive?," J. Aizen-berg, Gelsympo2012-Adaptive Hybrid Architectures Conference, Tsukuba, Ibaraki, Japan, October 9-11, 2012. [Plenary speaker]
12. "Non-Fouling Dynamic Surfaces," J. Aizenberg, Symposium on Fusion Materials, University of Tokyo, Tokyo, Japan, Oct 7-8, 2012. [Plenary speaker]
13. "Liquid infused slippery surface coatings on metals for anti-ice applications," P. Kim, T.-S. Wong, J. Alvarenga, M. J. Kreder, W. E. Adorno-Martinez, J. Aizenberg, EPNanoNet Sum-mit 2012, Houston, TX, September 2012.
14. "Liquid-Infused Porous Materials," J. Aizenberg, Twente/MESA Symposium, Amsterdam, Netherlands, September 20, 2012. [Keynote speaker]
15. "Slippery Ice-phobic Coatings on Aluminum," P. Kim, T.-S. Wong, J. Alvarenga, M. J. Kreder, J. Aizenberg, 8th International Symposium on Contact Angle, Wettability, and Ad-hesion, Quebec City, Quebec, Canada, June 2012.
16. "Dynamic, Adaptive Materials: Lessons from Nature," J. Aizenberg, Gordon Research Con-ference on Bioinspired Materials, Davidson College, Davidson, NC, June 24-27, 2012.
17. "Bio-Inspired Slippery Anti-Frost Coating on Aluminum for Energy Efficient Refrigerator Heat Exchangers," P. Kim, W. E. Adorno-Martinez, J. Alvarenga, J. Aizenberg, MRS Spring Meeting, San Francisco, CA, April 2012.
18. "Patterned and Controllable pH-Responsive Actuation of Polymer Microstructures," L. D. Zarzar, X. He, Q. Liu, P. Kim, Z. Suo, J. Aizenberg, ACS National Meeting, San Diego, CA, March 2012.
19. "Steering Nanostructures: Controlling Self-Assembly of Bio-inspired Nanofibers," S. H. Kang, J. Aizenberg, ACS Spring National Meeting, San Diego, CA, March 2012.
20. "Buckling-induced Planar Chirality of Porous Elastic Structure," J. Shim, S. Shan, S. H. Kang, P. Wang, B. R. Chen, J. Aizenberg, APS March Meeting, Boston, MA, March 2012.
21. "Buckling-induced Tunable Chirality in Rationally-Designed Surface-Attached Cellular Structures," S. Shan, S. H. Kang, W. Noorduin, M. Khan, K. Bertoldi, J. Aizenberg, APS March Meeting, Boston, MA, March 2012.
22. "Capillary-Induced Self-Organization of Soft Pillar Arrays into Moiré Patterns by Dynamic Feedback Process," S. H. Kang, N. Wu, A. Grinthal, J. Aizenberg, APS March Meeting, Bos-ton, MA, March 2012.

D.P. Holmes

23. D.P. Holmes, "Using Thin Films of Rubber to Move Thin Films of Fluid," New England Complex Fluids Workshop, Yale University, 2013.
24. B. Tavakol, M. Bozlar, G. Froehlicher, H.A. Stone, I. Aksay, and D.P. Holmes, "Buckling In-stability of Dielectric Elastomeric Plates for Soft, Bio-Compatible Microfluidic Pumps," So-ciety of Engineering Science 50th Annual Technical Meeting, 2013.
25. B. Tavakol, M. Bozlar, G. Froehlicher, C. Punckt, H.A. Stone, I. Aksay, and D.P. Holmes, "Buckling Instability of Dielectric Elastomeric Plates for Soft, Bio-Compatible Microfluidic Pumps," Bulletin of the American Physical Society, 58, 2013.
26. B. Tavakol, D.P Holmes, G. Froehlicher, and H.A. Stone, "Control and Manipulation of Fluid Flow Using Elastic Deformations," Bulletin of the American Physical Society, 57, 2013.
27. D.P. Holmes, "Control and Manipulation of Fluid Flow using Elastic Deformations," OC-CAM - Oxford University, 2012.

Z. Suo

28. Z. Suo "Soft active materials." Max Plank Institute of Dynamics and Self-Organization, Gottingen, Germany, May 30, 2012.
29. Z. Suo "Active gels—when mechanics meets chemistry." Institute of Polymer Science, Karlsruhe Institute of Technology, Germany, April 16, 2012.
30. Z. Suo "Soft Active Materials—when mechanics meets chemistry." invited session on De-formation and Fracture of Soft Materials, 2012 March Meeting of the American Physical So-ciety, March 1, 2012.

31. May 30, 2013. “Highly stretchable and tough hydrogels.” Seminar, ESPCI ParisTech.
32. May 24, 2013. “Soft active materials and soft machines.” Seminar, ESPCI ParisTech.
33. April 24, 2013. “Soft active materials and soft machines.” Seminar, Chemical and Biological Engineering Department, Princeton University.
34. April 3, 2013. “Highly stretchable and tough hydrogels.” Invited talk. Symposium NN Multi-functional Biomaterials. MRS Spring Meeting. San Francisco.
35. March 22, 2013. “Electromechanical instability in soft materials: theory, experiments and applications.” Invited session on Elastic instabilities and pattern formation in structureless solids. American Physical Society March Meeting, Baltimore. Invited by Benny Davidovitch.
36. March 15, 2013. “Mechanics of hydrogels.” 54th New England Complex Fluids Workshop. Yale University.
37. February 6, 2013. “Extremely stretchable and tough hydrogels.” Squishy Physics Seminars.
38. January 22, 2013. “Soft generators that harvest energy from renewable sources.” Arthur Newell Talbot Lecture. Invited by Placid Ferreira, Head of the Department of Mechanical Science and Engineering, The University of Illinois, Urbana-Champaign.
39. January 9, 2013. “Extremely stretchable and tough hydrogels.” Invited talk. Gordon Research Conferences on Macromolecular Materials. Ventura.
40. December 15, 2012. “Artificial muscles made of dielectric elastomers.” Invited talk. Ad-vanced Institute of Science and Technology (AIST), Osaka, Japan.
41. December 13, 2012. “Energy harvesting using dielectric elastomers.” Invited talk. Section on Energy Conversion, 9th International Polymer Conference, Society of Polymer Science, Ja-pan. Kobe, Japan.
42. November 12, 2012. “Normal and extreme mechanical behavior of hydrogels: theory and ex-periments” Keynote. Symposium on hydrogels. ASME Winter Annual Meeting, Houston.
43. November 12, 2012. “Soft materials and soft machines.” Robert Henry Thurston Lecture Award. American Society of Mechanical Engineers (ASME). Houston.
44. October 16, 2012. “Theory of dielectric elastomers.” Training School on Dielectric EAPs in Neuchâtel.
45. October 10, 2012. “Active gels.” A symposium in honor of Professor Zdenek Bazant on the occasion of his 75 Birthday. Society of Engineering Sciences.
46. August 22, 2012. “Theory and experiments of dielectric elastomers.” IUTAM Congress, Bei-jing.
47. June 15, 2012. “Soft active materials—when mechanics meets chemistry.” EPFL, Switzer-land.
48. May 30, 2012. “Soft active materials.” Max Plank Institute of Dynamics and Self-Organization, Gottingen.
49. April 16, 2012. “Active gels—when mechanics meets chemistry.” Institute of Polymer Sci-ence, Karlsruhe Institute of Technology.
50. March 1, 2012. “Soft Active Materials—when mechanics meets chemistry.” invited session on Deformation and Fracture of Soft Materials, 2012 March Meeting of the American Physi-cal Society.

Number of Presentations: 50.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

1. D.P. Holmes, J.S. Hochgraf, M. Libuit. "Active Shear Thickening Fluid Composite Orthosis," 2012.
2. H.A. Stone, D.P. Holmes, G. Froehlicher. "Control and Manipulation of Fluid Flow via Elas-tic Deformations," 2011.
3. R.M. Martinez and G.M. Whitesides, "Programmable Paper-Elastomer Composites as Pneu-matic Actuators," PROV Priority, 2012.
4. R.M. Martinez and G.M. Whitesides, "Apparatus, Systems, and Method for Providing Fabric Elastomer Composites as Pneumatic Actuators," PCT, 2013.
5. J.-Y. Sun, X. Zhao, W.R.K. Illeperuma, K.H. Oh, D.J. Mooney, J.J. Vlassak, Z. Suo, "Inter-penetrating networks with covalent and ionic crosslinks for extremely stretchable and tough hydrogels," 2012.
6. J. Aizenberg and P. Kim, "Hierarchical Structured Surfaces To Control Wetting Characteris-tics" PCT/US11/44553 2011.

Patents Awarded

Awards

J. Aizenberg

- Fellow of the American Physical Society
- R&D 100 Award – Slippery liquid-infused porous surfaces (SLIPS)
- Distinguished Franklin Award in Chemistry - Rice University
- Best poster award, Aspen Soft Matter conference "Growth and Form: Pattern Formation in Biology"
- SLIPS selected as #1 in 14 Best Inventions using Biomimicry in 2011 by Treehugger and top biomimicry invention by RobAid and Greenbiz.
- Best Poster Award nomination, Materials Research Society
- Gold Medal, Materials Research Society Graduate Student Award
- AkzoNobel Graduate Research Award
- Poster award, second place - NSF Workshop and Freund Symposium on Future Directions in Mechanics Research
- W.J. Chute Distinguished Lectureship in Chemistry, Dalhousie University
- Molecular Foundry Distinguished Lectureship in Chemistry, Lawrence Berkeley National Labs
- Eastman Chemical Company Award Lectureship, Goodyear Polymer Center, University of Akron
- Distinguished Lectureship, Bio-X "Frontiers in Interdisciplinary Biosciences," Stanford University
- Jerome B. Cohen Distinguished Lectureship, Northwestern University
- Distinguished Naff Lectureship, Kentucky University
- Science as Art competition, second place - Materials Research Society
- Science Magazine Photography Competition
- Poster Award, Materials Research Society

D. P. Holmes

- ASEE Ferdinand P. Beer and E. Russell Johnston, Jr. Outstanding New Mechanics Educator

G. M. Whitesides

- Benjamin Franklin Medal in Chemistry (Franklin Foundation) (2009)
- Fast Company Magazine. 100 Most Creative People in Business (2009)
- Dreyfus Award in Materials Chemistry (Dreyfus Foundation) (2009)
- Popular Mechanics Magazine: "Breakthrough Award, 2009"
- IKCOC Prize (International Kyoto Conference on New Aspects of Organic Chemistry) (2009)
- Othmer Gold Medal (Chemical Heritage Foundation) (2010)
- Phi Beta Kappa (honorary member, Harvard University) (2010)
- King Feisal Prize in Science (Saudi Arabia) (2011)
- F. A. Cotton Award (Texas ACS Section) (2011)
- Priestley Award (Dickenson College) (2011)
- Honorary Doctor of Science, University of Windsor, Canada (2010)
- Honorary Doctor of Science, McGill University, Canada (2010)
- Honorary Doctor of Science, Université Libre de Bruxelles, Belgium (2010)
- Honorary Doctor of Science, Aarhus University, Denmark (2011)
- Honorary Doctor of Science, Freie Universitaet Berlin, Germany (2012);
- Honorary Doctor of Science, Université Libre de Bruxelles, Belgium (2012)

H. A. Stone

- Kobayashi-Morrison Lecture, Department of Mechanical Engineering, University of Washington, May 2012
- Disquisitiones Mechanicae, Mechanical Science & Engineering, Univ. Illinois, Febru-ary 2012
- Visiting Professor, Institut Jean le Rond dAlembert, Paris, July 2011.
- Visiting Professor, FAST Laboratory, Paris, July 2011.
- Elected to membership in the American Academy of Arts and Sciences, April 2011.
- Engineering Council Teaching Award, School of Engineering and Applied Sciences, Princeton University, February 2011.
- BSL Lecture, Dept of Chemical and Biological Engineering, University of Wisconsin, May 2011.
- Pollack Lectures, Technion – Israel Institute of Technology, Haifa Israel, March 2011.
- Liviu Librescu Memorial Lecture, Department of Engineering Science and Mechanics, Virginia Tech, March 2011.
- Civil Engineering and Geological Sciences, Notre Dame, Edison Distinguished Lecture, April 2011.
- Department of Chemical Engineering and Applied Chemistry, Lectures at the Leading Edge, University of Toronto, April 2011.
- Invited speaker, Distinguished Seminar Series, Department of Chemical Engineering, Imperial College, London, January 2011.
- Visiting Professor, Chaire Saint Gobain, ESPCI, Paris, July 2010
- H.A. Stone, Carl J. Rees Distinguished Lecturer, Dept Mathematical Sciences, U. Delaware, April 2010
- H.A. Stone, DiPrima Lecture, Dept of Mathematical Sciences, Rensselear Polytechnic Institute, April 2010
- H.A. Stone, Haythornthwaite Foundation Lecture, College of Engineering, Temple University, January 2010
- H.A. Stone, Orsted Lecture, Technical University of Denmark (DTU), November 2009

I. A. Aksay

- Turkish Academy of Sciences (TÜBA), 2010
- National Academy of Engineering, February 2010

- Partner University Fund, French Embassy, July 2010

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
D. J. Bozym	1.00	
Andrew G. Hsieh	1.00	
Linda Jan	1.00	
Lihua Jin	1.00	
Lidiya Mishchenko	1.00	
Shuyang Pan	1.00	
Michael A. Pope	1.00	
Joseph D. Roy-Mayhew	1.00	
Behrouz Tavakol	0.50	
New Entry	0.00	
FTE Equivalent:	**8.50**	
Total Number:	**10**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Jabulani Barber	0.00
Michael Bozlar	0.50
Rebecca Cademartiri	0.75
Won Jae Choi	0.10
Frederique Deiss	0.50
Camille Duprat	0.00
Yuhang Hu	0.50
Pilnam Kim	0.50
Sen Wai Kwok	0.25
Xinyu Liu	0.00
Ramses V. Martinez	0.25
Steve Morin	0.25
Rui Nunes	0.50
Matthieu Roche	0.00
Umut Salman	0.50
Yueyang Shen	0.20
Karen Simon	0.75
Ju-Hee So	0.25
Siowling Soh	0.25
Adam Stokes	0.25
Alok S. Tayi	0.50
Martin Thuo	0.25
Simon Tricard	0.50
Jian Zhu	0.00
FTE Equivalent:	**7.55**
Total Number:	**24**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Joanna Aizenberg	0.05	
Ilhan A. Aksay	0.05	Yes
Douglas P. Holmes	0.50	
Jean-Herve Prevost	0.05	
Howard A. Stone	0.00	Yes
Zhigang Suo	0.10	Yes
George M. Whitesides	0.02	Yes
FTE Equivalent:	**0.77**	
Total Number:	**7**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Wilmer E. Adrono-Martinez	0.00	Chemistry
Daniel Flagg	0.00	Chemical Engineering
John S. Hochgraf	0.00	Chemical Engineering
Matthew Libuit	0.00	Chemical Engineering
Varsh Peddireddy	0.00	Chemical Engineering
Amanda Sagastegui	0.00	Chemical and Biological Engineering
Andreas K. Sakellaris	0.00	Chemical and Biological Engineering
Jas A. Sanghera	0.00	Chemical Engineering
Tarun Sinha	0.00	Civil and Environmental Engineering
Audrey R. Zak	0.00	Chemical and Biological Engineering
FTE Equivalent:	**0.00**	
Total Number:	**10**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 10.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 10.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 5.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 9.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 1.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 2.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Sung Hoon Kang
Lidiya Mishchenko
Shuyang Pan
Lauren Zarzar
Total Number: 4

Names of other research staff

NAME	PERCENT_SUPPORTED
Daniel M. Dabbs	0.30
T. J. Martin	0.25
David L. Milius	0.50
FTE Equivalent:	**1.05**
Total Number:	**3**

Sub Contractors (DD882)

Inventions (DD882)

5 **Active Shear Thickening Fluid Composite Orthosis**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: D. P. Holmes

5f-1a: Virginia Tech

5f-c:

5 **Apparatus, Systems, and Method for Providing Fabric Elastomer Composites as Pneumatic Actuators**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: G. M. Whitesides

5f-1a: Harvard University

5f-c:

5 **Control and Manipulation of Fluid Flow via Elastic Deformations**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: D. P. Holmes

5f-1a: Virginia Tech

5f-c:

5 **Hierarchical Structured Surfaces To Control Wetting Characteristics**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) Y

Foreign Countries of application (5g-2):

5a: J. Aizenberg

5f-1a: Harvard University

5f-c:

5 **Interpenetrating networks with covalent and ionic crosslinks for extremely stretchable and tough hydrogels**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Z. Suo

5f-1a: Harvard University

5f-c:

5 **Programmable Paper-Elastomer Composites as Pneumatic Actuators**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: G. M. Whitesides

5f-1a: Harvard University

5f-c:

Scientific Progress

See Attachment.

Technology Transfer

Final Report
Cover Page
Princeton University
Princeton, New Jersey 08544

ANNUAL REPORT SUBMITTED TO: Army Research Office

TITLE OF GRANT: Innovative Design and Processing of Multi-Functional Adaptive Structural Materials

GRANT NUMBER: W911NF-09-1-0476

PRINCIPAL INVESTIGATOR:

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Materials Science (AMSRD-ARL-RO-EM)

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TOTAL COST OF PROJECT:

REPORT PERIOD: 09/01/2009 – 05/31/2013

DATE SUBMITTED: 09/03/2013

Keywords: multi-functional materials, graphene, adaptive materials, nanocomposites

INNOVATIVE DESIGN AND PROCESSING OF MULTI-FUNCTIONAL ADAPTIVE STRUCTURAL MATERIALS
GRANT NUMBER: W911NF-09-1-0476

Ilhan A. Aksay, Princeton University, Principal Investigator

ABSTRACT

Our project on adaptive structural materials began with bone as a source of inspiration for adaptive materials systems. Examining the structure of natural bone leads to the five guiding principles for our research: (i) load bearing by hierarchically porous materials; (ii) adaptive, sensing load and supplying mass to reinforce at load-bearing sites through material deposition and dissolution; (iii) transport of materials using fluid flow through low density porous systems; (iv) energy to drive processes taken from storage sites, which are replenished by internal or external energy generation; (v) mechanisms, which are not fully understood for bone, but knowing the fundamental mechanisms allows these to be adjusted for application to synthetic systems. The problem as defined in the third year of the program was how to change soft materials into hard structures reversibly, in response to load or other environmental stresses. The approaches we used in the third year of the program include (i) reversible jamming, layering, welding and/or percolation; (ii) dissipative materials; and (iii) granular chemistry.

PUBLICATIONS AND MANUSCRIPTS

Papers Published in Peer-Reviewed Journals

1. J. Aizenberg, "New nanofabrication strategies: Inspired by biomineralization", *MRS Bull*., **2010**, *35*, 323-330.
2. A. R. Abate, L. Han, L. H. Jin, Z. G. Suo, D. A. Weitz, "Measuring the elastic modulus of microgels using microdrops," *Soft Matter*, **2012**, *8*, 10032-10035. DOI: 10.1039/c2sm26108a.
3. A. Belotserkovets, J.H. Prevost, "Thermoporoelastic response of a fluid-saturated porous sphere: An analytical solution," *Intern. J. Eng. Sci.*, **2011**, *49* 1415-1423. DOI: 10.1016/j.ijengsci.2011.05.017.
4. M. Bozlar, C. Punckt, S. Korkut, J. Zhu, C. C. Foo, Z. G. Suo, I. A. Aksay, "Dielectric Elastomer Actuators with Elastomeric Electrodes," *Appl. Phys. Lett.*, **2012**, *101*, 091907. DOI: 10.1063/1.4748114.
5. S. Q. Cai, K. Bertoldi, H. M. Wang, Z. G. Suo, "Osmotic collapse of a void in an elastomer: breathing, buckling and creasing," *Soft Matter*, **2010**, *6*, 5770-5777. DOI: 10.1039/c0sm00451k.
6. S. Q. Cai, D. Y. Chen, Z. G. Suo, R. G. Hayward, "Creasing instability of elastomer films," *Soft Matter*, **2012**, *8*, 1301-1304. DOI: 10.1039/c2sm06844c.
7. S. Cai, Z. Suo, "Equations of state for ideal elastomeric gels," *EPL*, **2012**, *97*, 34009. DOI: 10.1209/0295-5075/97/34009.
8. E.P. Chan, Y. Hu, P.M. Johnson, Z. Suo, C.M. Stafford, "Spherical indentation testing of poroelastic relaxations in thin hydrogel layers," *Soft Matter*, **2012**, *8*, 1492-1498. DOI: 10.1039/c1sm06514a.
9. W. Choi, M. Hashimoto, A. K. Ellerbee, X. Chen, K. J. M. Bishop, P. Garstecki, H. A. Stone, G. M. Whitesides, "Bubbles navigating through networks of microchannels," *Lab Chip*, **2011**, *11*, 3970-3978. DOI: 10.1039/c1lc20444k.
10. D.M. Dabbs, I.A. Aksay, "Multifunctional and Low-Density Inorganic Nanocomposites," *JOM*, **2012**, *64* [2] 226-233. DOI: 10.1007/s11837-012-0236-1.

11. D. Du, Z. X. Zou, Y. S. Shin, J. Wang, H. Wu, M. H. Engelhard, J. Liu, I. A. Aksay, Y. H. Lin, "Sensitive Immunosensor for Cancer Biomarker Based on Dual Signal Amplification Strategy of Graphene Sheets and Multienzyme Functionalized Carbon Nanospheres," *Anal. Chem.*, **2010**, *82*, 2989-2995. DOI: 10.1021/ac100036p.
12. C.C. Foo, S. Cai, S.J.A. Koh, S. Bauer, Z. Suo, "Model of dissipative dielectric elastomers," *J. Appl. Phys.*, **2012**, *111*, 034102. DOI: 10.1063/1.3680878.
13. C.C. Foo, S.J.A. Koh, C. Keplinger, R. Kaltseis, S. Bauer, Z. Suo, "Performance of dissipative dielectric elastomer generators," *J. Appl. Phys.*, **2012**, *111*, 094107. DOI: 10.1063/1.4714557.
14. P. Fratzl, F.D. Fischer, J. Svoboda, J. Aizenberg, "A kinetic model of the transformation of a micropatterned amorphous precursor into a porous single crystal", *Acta Biomater*. **2010**, *6*, 1001–1005. DOI: 10.1016/j.actbio.2009.09.002.
15. B. Hatton, V. Kitaev, D. Perovic, G. Ozin, J. Aizenberg, "Low-Temperature Synthesis of Nanoscale Silica Multilayers – Atomic Layer Deposition in a Test Tube" *J. Mater. Chem.* **2010**, *20*, 6009 - 6013. DOI: DOI: 10.1039/c0jm00696c.
16. B. Hatton, L. Mishchenko, S. Davis, K.H. Sandhage, J. Aizenberg, "Assembly of large-area, highly ordered, crack-free inverse opal films", *Proc. Nat. Acad. Sci. USA*, **2010**, *107*(23), 10354-10359. DOI: 10.1073/pnas.1000954107.
17. W. Holloway, J.M. Aristoff, H.A. Stone, "Imbibition of concentrated suspensions in capillaries," *Phys. Fluids*, **2011**, *23*, 081701.
18. D. P. Holmes, M. Roche, T. Sinha, H. A. Stone, "Bending and twisting of soft materials by non-homogenous swelling," *Soft Matter*, **2011**, 5188-5193. DOI: 10.1039/c0sm01492c.
19. D.P. Holmes, B. Tavakol, G. Froehlicher, and H.A. Stone, "Control and Manipulation of Microfluidic Fluid Flow *via* Elastic Deformations," *Soft Matter*, **2013**, *9*, 7049-7053. DOI: 10.1039/c3sm51002f.
20. Y. Hu, E.P. Chan, J.J. Vlassak, Z. Suo, "Poroelastic relaxation indentation of thin layers of gels," *J. Appl. Phys.*, **2011**, *110*, 086103. DOI: 10.1063/1.3647758.
21. Y. Hu, Z. Suo, "Viscoelasticity and poroelasticity in elastomeric gels," *Acta Mechanica Solida Sinica*, **2012**, *25*, 441-458.
22. Y. Hu, X. Chen, G. M. Whitesides, J. J. Vlassak, Z. Suo, "Indentation of Polydimethylsiloxane Submerged in Organic Solvents," *J. Mater. Res.*, **2011**, *26*, 785-795. DOI: 10.1557/jmr.2010.35.
23. Y. Hu, J.-O. You, D.T. Auguste, Z. Suo, J.J. Vlassak, "Indentation: a simple, nondestructive method for characterizing the mechanical and transport properties of pH-sensitive hydrogels," *J. Mater. Res.*, **2012**, *27*, 152-160. DOI: 10.1557/jmr.2011.368.
24. R. Huang, Z. Suo, "Electromechanical phase transition in dielectric elastomers," *Proc. Roy. Soc. A*, **2012**, *468*, 1014-1040. DOI: 10.1098/rspa.2011.0452.
25. L. Jan, C. Punckt, B. Khusid, I. A. Aksay, "Directed motion of colloidal particles in galvanic microreactor," *Langmuir*, **2013**, *29* (8), 2498-2505. DOI: 10.1021/la303757a.
26. L. Jin, S. Cai, Z. Suo, "Creases in soft tissues generated by growth," *EPL*, **2011**, *95*, 64002. DOI: 10.1209/0295-5075/95/64002.
27. R. Kaltseis, C. Keplinger, R. Baumgartner, M. Kaltenbrunner, T. Li, P. Machler, R. Schwodiauer, Z. Suo, S. Bauer, "Method for measuring energy generation and efficiency of dielectric elastomer generators," *Appl. Phys. Lett.*, **2011**, *99*, 162904. DOI: 10.1063/1.3653239.

28. S. H. Kang, S. Shan, W. L. Noorduin, M. Khan, J. Aizenberg, K. Bertoldi, "Buckling-induced Reversible Symmetry Breaking and Amplification of Chirality using Supported Cellular Structures," *Adv. Mater*. **2013**, 25, 3380-3385. DOI: 10.1002/adma.201300617
29. C. Keplinger, T. Li, R. Baumgartner, Z. Suo, S. Bauer, "Harnessing snap-through instability in soft dielectrics to achieve giant voltage-triggered deformation," *Soft Matter*, **2011**, *8*, 285-288. DOI: 10.1039/c1sm06736b.
30. C. Keplinger, R. Baumgartner, S. Bauer, W. Yang, Z. G. Suo, "Giant voltage-induced deformation in dielectric elastomers near the verge of snap-through instability," *J. Mech. Phys. Sol.*, **2013**, *61*, 611-628. DOI: 10.1016/j.jmps.2012.09.006.
31. C. Keplinger, J.-Y. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides, Z. G. Suo, "Stretchable, Transparent, Ionic Conductors," *Science*, **2013**, *341*, 984-987. DOI: 10.1126/science.1240228.
32. P. Kim, M. Abkarian, H. A. Stone, "Hierarchical folding of elastic membranes under biaxial compressive stress," *Nat. Mater.*, **2011**, *10*, 952-957.
33. P. Kim, W. E. Adorno-Martinez, M. Khan, J. Aizenberg, "Enriching libraries of high-aspect-ratio micro- or nanostructures by rapid, low-cost, benchtop nanofabrication," *Nat. Protocols*, **2012**, *7*, 311-327. DOI: 10.1038/nprot.2012.003.
34. P. Kim, C. Duprat, S. S. H. Tsai, H. A. Stone, "Selective Spreading and Jetting of Electrically Driven Dielectric Films," *Phys. Rev. Lett.*, **2011**, *107*, 034502. DOI: 10.1103/PhysRevLett.107.034502.
35. P. Kim, A.K Epstein, M. Khan, L.D. Zarzar, D.J. Lipomi, G.M. Whitesides, J. Aizenberg, "Structural Transformation by Electrodeposition on Patterned Substrates (STEPS) – A New Versatile Nanofabrication Method," *Nano Lett.* **2012**, *12*, 527-533. DOI: 10.1021/nl200426g.
36. P. Kim, L.D. Zarzar, X. He, A. Grinthal, J. Aizenberg, "Hydrogel-Actuated Integrated Responsive Systems (HAIRS): Moving towards Adaptive Materials," *Curr. Opin. Solid State Mater. Sci.*, **2011**, *15*, 236-245.
37. P. Kim, L.D. Zarzar, X. Zhao, A. Sidorenko, J. Aizenberg "Microbristle in Gels: Toward All-Polymer Reconfigurable Hybrid Surfaces" *Soft Matter*, **2010**, *6* [4], 750-755.
38. M. Kollosche, J. Zhu, Z. Suo, G. Kofod, "Complex interplay of nonlinear processes in dielectric elastomers," *Phys. Rev. E*, **2012**, *85*, 051801. DOI: 10.1103/PhysRevE.85.051801.
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44. R.V. Martinez, C.R. Fish, X. Chen, G.M. Whitesides, "Elastomeric Origami: Programmable Paper-Elastomer Composites as Pneumatic Actuators," *Adv. Func. Mater.*, **2012**, *22*, 1376-1384. DOI: 10.1002/adfm.201102978.
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57. Z. Suo, "Mechanics of stretchable electronics and soft machines," *MRS Bull.*, **2012**, *37*, 218-225. DOI: 10.1557/mrs.2012.32.
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Metal Oxide-Graphene Nanocomposites for Electrochemical Energy Storage," *ACS Nano*, **2010**, *4*, 1587-1595. DOI: 10.1021/nn901819n.
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63. T.-S. Wong, S. Hoon Kang, S.K.Y. Tang, E.J. Smythe, B.D. Hatton, A. Grinthal, J. Aizenberg, "Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity," *Nature*, **2011**, *477*, 443-447. DOI: 10.1038/nature10447.
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65. L. Yan, C. Punckt, I.A. Aksay, W. Mertin, G. Bacher, "Local Voltage Drop in a Single Functionalized Graphene Sheet Characterized by Kelvin Probe Force Microscopy," *Nano Lett.*, **2011**, *11*, 3543-49.
66. N. Zalachas, S. Q. Cai, Z. G. Suo, Y. Lapusta, "Crease in a ring of a pH-sensitive hydrogel swelling under constraint," *Int. J. Sol. Struct.*, **2013**, *50*, 920-927. DOI: 10.1016/j.ijsolstr.2012.11.015.
67. J. Zhu, M. Kollosche, T. Q. Lu, G. Kofod, Z. G. Suo, "Two types of transitions to wrinkles in dielectric elastomers," *Soft Matter*, **2012**, *8*, 8840-8846. DOI: 10.1039/c2sm26034d.

Papers Published in Non-Peer Reviewed Journals

None during report period.

Presentations at Meetings, but not Published in Proceeding (2012-2013)

J. Aizenberg

1. "Novel Self-Regulating Homeostatic Materials," M. Aizenberg, X. He, J. Aizenberg, Frontiers in Macromolecular and Supramolecular Science, Bucharest, Romania, June 7-14, 2013.
2. "Responsive, Self-regulated Systems: From Molecules to Devices," J. Aizenberg, Gordon Research Conference (GRC) on Self-Assembly & Supramolecular Chemistry, Les Diablerets, Switzerland, May 5-10, 2013.
3. "Slippery When Wet: Liquid-Infused Nanostructured Omni-Repellent Coatings and Biomedical Applications" P. Kim, New England Bioscience Society 2013 Annual Meeting, Harvard Medical School, Boston, MA, April 27, 2013.
4. "Rational Design of Omni-Repellent Liquid-Infused Nanostructured Surfaces and Their Manufacturable Coating Methods on a Wide Range of Materials," P. Kim, M. J. Kreder, J. Alvarenga, J. Aizenberg, Smart Coatings 2013, Orlando, FL, February 20, 2013.
5. 'Homeostatic Materials," M. Aizenberg, X. He, J. Aizenberg, Advanced Materials and Nanotechnology (AMN)-6 Conference, Auckland, New Zealand, February 11-February 15, 2013. [Keynote speaker]
6. 'Everything SLIPS: Design of Novel Omniphobic Materials," J. Aizenberg, Advanced Materials and Nanotechnology (AMN)-6 Conference, Auckland, New Zealand, February 11-February 15, 2013. [Keynote speaker]
7. "Slippery Materials that Repel Everything," J.Aizenberg, Materials Research Society Fall 2012 meeting, Boston, MA, November 27, 2012.
8. "Evaporation-Induced Self-Organization of Polymer Nanorod Arrays: When Structured Solids Met a Liquid," S. H. Kang, B. Pokroy, N. Wu, L. Mahadevan, J. Aizenberg, 49th Society of Engineering Science Meeting, Atlanta, GA, October 2012.

9. "Liquid-Infused Nanostructured Surfaces with Extreme Anti-Ice and Anti-Frost Performance," P. Kim, T.-S. Wong, J. Alvarenga, M. J. Kreder, W. E. Adorno-Martinez, J. Aizenberg, NIST/Industry Polymer Surface/Interface (PSI) Consortium, Wallingford, CT, October 2012.
10. "Autonomic Dynamic Materials Displaying Chemo-mechano-chemical Self-regulation," M. Aizenberg, X. He, O. Kuksenok, L. D. Zarzar, A. Shastri , A. C. Balazs, J. Aizenberg, Gelsympo2012-Adaptive Hybrid Architectures Conference, Tsukuba, Ibaraki, Japan, October 9-11, 2012.
11. "Towards Dynamic Hybrid Architectures: Or Can We Make Materials Adaptive?," J. Aizenberg, Gelsympo2012-Adaptive Hybrid Architectures Conference, Tsukuba, Ibaraki, Japan, October 9-11, 2012. [Plenary speaker]
12. "Non-Fouling Dynamic Surfaces," J. Aizenberg, Symposium on Fusion Materials, University of Tokyo, Tokyo, Japan, Oct 7-8, 2012. [Plenary speaker]
13. "Liquid infused slippery surface coatings on metals for anti-ice applications," P. Kim, T.-S. Wong, J. Alvarenga, M. J. Kreder, W. E. Adorno-Martinez, J. Aizenberg, EPNanoNet Summit 2012, Houston, TX, September 2012.
14. "Liquid-Infused Porous Materials," J. Aizenberg, Twente/MESA Symposium, Amsterdam, Netherlands, September 20, 2012. [Keynote speaker]
15. "Slippery Ice-phobic Coatings on Aluminum," P. Kim, T.-S. Wong, J. Alvarenga, M. J. Kreder, J. Aizenberg, 8th International Symposium on Contact Angle, Wettability, and Adhesion, Quebec City, Quebec, Canada, June 2012.
16. "Dynamic, Adaptive Materials: Lessons from Nature," J. Aizenberg, Gordon Research Conference on Bioinspired Materials, Davidson College, Davidson, NC, June 24-27, 2012.
17. "Bio-Inspired Slippery Anti-Frost Coating on Aluminum for Energy Efficient Refrigerator Heat Exchangers," P. Kim, W. E. Adorno-Martinez, J. Alvarenga, J. Aizenberg, MRS Spring Meeting, San Francisco, CA, April 2012.
18. "Patterned and Controllable pH-Responsive Actuation of Polymer Microstructures," L. D. Zarzar, X. He, Q. Liu, P. Kim, Z. Suo, J. Aizenberg, ACS National Meeting, San Diego, CA, March 2012.
19. "Steering Nanostructures: Controlling Self-Assembly of Bio-inspired Nanofibers," S. H. Kang, J. Aizenberg, ACS Spring National Meeting, San Diego, CA, March 2012.
20. "Buckling-induced Planar Chirality of Porous Elastic Structure," J. Shim, S. Shan, S. H. Kang, P. Wang, B. R. Chen, J. Aizenberg, APS March Meeting, Boston, MA, March 2012.
21. "Buckling-induced Tunable Chirality in Rationally-Designed Surface-Attached Cellular Structures," S. Shan, S. H. Kang, W. Noorduin, M. Khan, K. Bertoldi, J. Aizenberg, APS March Meeting, Boston, MA, March 2012.
22. "Capillary-Induced Self-Organization of Soft Pillar Arrays into Moiré Patterns by Dynamic Feedback Process," S. H. Kang, N. Wu, A. Grinthal, J. Aizenberg, APS March Meeting, Boston, MA, March 2012.

D.P. Holmes

23. D.P. Holmes, "Using Thin Films of Rubber to Move Thin Films of Fluid," *New England Complex Fluids Workshop*, Yale University, 2013.
24. B. Tavakol, M. Bozlar, G. Froehlicher, H.A. Stone, I. Aksay, and D.P. Holmes, "Buckling Instability of Dielectric Elastomeric Plates for Soft, Bio-Compatible Microfluidic Pumps," *Society of Engineering Science* 50th Annual Technical Meeting, 2013.

25. B. Tavakol, M. Bozlar, G. Froehlicher, C. Punckt, H.A. Stone, I. Aksay, and D.P. Holmes, "Buckling Instability of Dielectric Elastomeric Plates for Soft, Bio-Compatible Microfluidic Pumps," *Bulletin of the American Physical Society*, **58**, 2013.
26. B. Tavakol, D.P Holmes, G. Froehlicher, and H.A. Stone, "Control and Manipulation of Fluid Flow Using Elastic Deformations," *Bulletin of the American Physical Society*, **57**, 2013.
27. D.P. Holmes, "Control and Manipulation of Fluid Flow using Elastic Deformations," *OCCAM* - Oxford University, 2012.

Z. Suo

28. Z. Suo "Soft active materials." Max Plank Institute of Dynamics and Self-Organization, Gottingen, Germany, May 30, 2012.
29. Z. Suo "Active gels—when mechanics meets chemistry." Institute of Polymer Science, Karlsruhe Institute of Technology, Germany, April 16, 2012.
30. Z. Suo "Soft Active Materials—when mechanics meets chemistry." invited session on Deformation and Fracture of Soft Materials, 2012 March Meeting of the American Physical Society, March 1, 2012.
31. May 30, 2013. "Highly stretchable and tough hydrogels." Seminar, ESPCI ParisTech.
32. May 24, 2013. "Soft active materials and soft machines." Seminar, ESPCI ParisTech.
33. April 24, 2013. "Soft active materials and soft machines." Seminar, Chemical and Biological Engineering Department, Princeton University.
34. April 3, 2013. "Highly stretchable and tough hydrogels." Invited talk. Symposium NN Multifunctional Biomaterials. MRS Spring Meeting. San Francisco.
35. March 22, 2013. "Electromechanical instability in soft materials: theory, experiments and applications." Invited session on Elastic instabilities and pattern formation in structureless solids. American Physical Society March Meeting, Baltimore. Invited by Benny Davidovitch.
36. March 15, 2013. "Mechanics of hydrogels." 54th New England Complex Fluids Workshop. Yale University.
37. February 6, 2013. "Extremely stretchable and tough hydrogels." Squishy Physics Seminars.
38. January 22, 2013. "Soft generators that harvest energy from renewable sources." Arthur Newell Talbot Lecture. Invited by Placid Ferreira, Head of the Department of Mechanical Science and Engineering, The University of Illinois, Urbana-Champaign.
39. January 9, 2013. "Extremely stretchable and tough hydrogels." Invited talk. Gordon Research Conferences on Macromolecular Materials. Ventura.
40. December 15, 2012. "Artificial muscles made of dielectric elastomers." Invited talk. Advanced Institute of Science and Technology (AIST), Osaka, Japan.
41. December 13, 2012. "Energy harvesting using dielectric elastomers." Invited talk. Section on Energy Conversion, 9th International Polymer Conference, Society of Polymer Science, Japan. Kobe, Japan.
42. November 12, 2012. "Normal and extreme mechanical behavior of hydrogels: theory and experiments" Keynote. Symposium on hydrogels. ASME Winter Annual Meeting, Houston.
43. November 12, 2012. "Soft materials and soft machines." Robert Henry Thurston Lecture Award. American Society of Mechanical Engineers (ASME). Houston.
44. October 16, 2012. "Theory of dielectric elastomers." Training School on Dielectric EAPs in Neuchâtel.
45. October 10, 2012. "Active gels." A symposium in honor of Professor Zdenek Bazant on the occasion of his 75 Birthday. Society of Engineering Sciences.

46. August 22, 2012. “Theory and experiments of dielectric elastomers.” IUTAM Congress, Beijing.
47. June 15, 2012. “Soft active materials—when mechanics meets chemistry.” EPFL, Switzerland.
48. May 30, 2012. “Soft active materials.” Max Plank Institute of Dynamics and Self-Organization, Gottingen.
49. April 16, 2012. “Active gels—when mechanics meets chemistry.” Institute of Polymer Science, Karlsruhe Institute of Technology.
50. March 1, 2012. “Soft Active Materials—when mechanics meets chemistry.” invited session on Deformation and Fracture of Soft Materials, 2012 March Meeting of the American Physical Society.

Published in Non-Peer-Reviewed Conference Proceedings (excluding abstracts)

1. P. Kim, L.D. Zarzar, A.K. Epstein, J. Aizenberg “Biomimetic, Hierarchical, Multidimensional Patterning of Conductive Polymers on High-Aspect-Ratio Microstructures” PMSE Preprint, American Chemical Society (2010).

Published in Peer-Reviewed Conference Proceedings (excluding abstracts)

1. A.K. Epstein, J. Aizenberg. “Biomimetic Nanostructured Surfaces with Designer Mechanics and Geometry for Broad Applications”, In: *Biosurfaces and Biointerfaces*, edited by J.A. Garrido, E. Johnston, C. Werner, T. Boland (Mater. Res. Soc. Symp. Proc. Volume 1236E, Warrendale, PA, **2010**) Paper# 1236-SS09-07 [Invited paper].

Manuscripts Submitted to or not yet Published by Peer-Reviewed Journals

1. L. Jin, D. Chen, R. C. Hayward, Z. G. Suo. “Creases on the interface between two soft materials.” Submitted 2013.
2. M. A. Pope, I. A. Aksay, “Beyond the Quantum Capacitance Limit in Graphene-Based Double-layer Capacitors,” *Nature Materials*, submitted 2013.

Manuscripts in Preparation for Submission to Peer-Reviewed Journals

1. B. Tavakol, M. Bozlar, G. Froehlicher, H.A. Stone, I. Aksay, and D.P. Holmes, “Buckling of Dielectric Elastomeric Plates for Electrically Active Microfluidic Pumps.”
2. B. Tavakol, D.P. Holmes, G. Froehlicher, and H.A. Stone, “Extended Lubrication Theory.”
3. B. Tavakol, J.S. Hochgraf, V. Peddireddy, M. Libuit, J.A. Sanghera, and D.P. Holmes, “Soft-Hard Material Transitions *via* Complex Fluids.”.
4. G. M. Whitesides, *et al.*, “Reconfigurable composites enabled by vacuum-based jamming.”
5. G. M. Whitesides, *et al.*, “Discrete jamming in crushable media.”
6. G. M. Whitesides, *et al.*, “Multi-staged mechanical modulus of layered composites.”
7. G. M. Whitesides, *et al.*, “Fabric-based strain sensors and switches to control the flow of fluids, electronic current and light.”
8. A. M. Pires, D. M. Dabbs, I. A. Aksay, “Mechanical properties of L_3-templated nanostructured silica fibers.”
9. H. Sai, D. M. Dabbs, I. A. Aksay, “Mechanical properties of L_3-templated nanostructured silica”.
10. S. Pan, S. E. Sanborn, L. J. Gibbons, E. J. Siochi, J.-H. Prevost, R. K. Prud’homme, I. A. Aksay, “Enhanced Distributed Deformation in Graphene-Silicone Nanocomposites.”
11. M. Bozlar, K. S. Sallah, M. Alifierakis, S. Korkut, C. Punckt, I. A. Aksay, “Comparison of Graphene and Carbon Black as Electrically Conducting Reinforcements of Silicone Rubber.”

Books

1. "No Small Matter: Science on the Nanoscale," G.M. Whitesides and F. Frankel, Belknap Press, 2009.

HONORS AND AWARDS

J. Aizenberg
- Fellow of the American Physical Society
- R&D 100 Award – Slippery liquid-infused porous surfaces (SLIPS)
- Distinguished Franklin Award in Chemistry - Rice University
- Best poster award, Aspen Soft Matter conference "Growth and Form: Pattern Formation in Biology"
- SLIPS selected as #1 in 14 Best Inventions using Biomimicry in 2011 by Treehugger and top biomimicry invention by RobAid and Greenbiz.
- Best Poster Award nomination, Materials Research Society
- Gold Medal, Materials Research Society Graduate Student Award
- AkzoNobel Graduate Research Award
- Poster award, second place - NSF Workshop and Freund Symposium on Future Directions in Mechanics Research
- W.J. Chute Distinguished Lectureship in Chemistry, Dalhousie University
- Molecular Foundry Distinguished Lectureship in Chemistry, Lawrence Berkeley National Labs
- Eastman Chemical Company Award Lectureship, Goodyear Polymer Center, University of Akron
- Distinguished Lectureship, Bio-X "Frontiers in Interdisciplinary Biosciences," Stanford University
- Jerome B. Cohen Distinguished Lectureship, Northwestern University
- Distinguished Naff Lectureship, Kentucky University
- Science as Art competition, second place - Materials Research Society
- Science Magazine Photography Competition
- Poster Award, Materials Research Society

D. P. Holmes
- ASEE Ferdinand P. Beer and E. Russell Johnston, Jr. Outstanding New Mechanics Educator

G. M. Whitesides
- Benjamin Franklin Medal in Chemistry (Franklin Foundation) (2009)
- Fast Company Magazine. 100 Most Creative People in Business (2009)
- Dreyfus Award in Materials Chemistry (Dreyfus Foundation) (2009)
- Popular Mechanics Magazine: "Breakthrough Award, 2009"
- IKCOC Prize (International Kyoto Conference on New Aspects of Organic Chemistry) (2009)
- Othmer Gold Medal (Chemical Heritage Foundation) (2010)
- Phi Beta Kappa (honorary member, Harvard University) (2010)
- King Feisal Prize in Science (Saudi Arabia) (2011)
- F. A. Cotton Award (Texas ACS Section) (2011)
- Priestley Award (Dickenson College) (2011)
- Honorary Doctor of Science, University of Windsor, Canada (2010)

- Honorary Doctor of Science, McGill University, Canada (2010)
- Honorary Doctor of Science, Université Libre de Bruxelles, Belgium (2010)
- Honorary Doctor of Science, Aarhus University, Denmark (2011)
- Honorary Doctor of Science, Freie Universitaet Berlin, Germany (2012);
- Honorary Doctor of Science, Université Libre de Bruxelles, Belgium (2012)

H. A. Stone

- Kobayashi-Morrison Lecture, Department of Mechanical Engineering, University of Washington, May 2012
- Disquisitiones Mechanicae, Mechanical Science & Engineering, Univ. Illinois, Febru-ary 2012
- Visiting Professor, Institut Jean le Rond dAlembert, Paris, July 2011.
- Visiting Professor, FAST Laboratory, Paris, July 2011.
- Elected to membership in the American Academy of Arts and Sciences, April 2011.
- Engineering Council Teaching Award, School of Engineering and Applied Sciences, Princeton University, February 2011.
- BSL Lecture, Dept of Chemical and Biological Engineering, University of Wisconsin, May 2011.
- Pollack Lectures, Technion – Israel Institute of Technology, Haifa Israel, March 2011.
- Liviu Librescu Memorial Lecture, Department of Engineering Science and Mechanics, Virginia Tech, March 2011.
- Civil Engineering and Geological Sciences, Notre Dame, Edison Distinguished Lecture, April 2011.
- Department of Chemical Engineering and Applied Chemistry, Lectures at the Leading Edge, University of Toronto, April 2011.
- Invited speaker, Distinguished Seminar Series, Department of Chemical Engineering, Imperial College, London, January 2011.
- Visiting Professor, Chaire Saint Gobain, ESPCI, Paris, July 2010
- H.A. Stone, Carl J. Rees Distinguished Lecturer, Dept Mathematical Sciences, U. Delaware, April 2010
- H.A. Stone, DiPrima Lecture, Dept of Mathematical Sciences, Rensselear Polytechnic Institute, April 2010
- H.A. Stone, Haythornthwaite Foundation Lecture, College of Engineering, Temple University, January 2010
- H.A. Stone, Orsted Lecture, Technical University of Denmark (DTU), November 2009

I. A. Aksay

- Turkish Academy of Sciences (TÜBA), 2010
- National Academy of Engineering, February 2010
- Partner University Fund, French Embassy, July 2010

PATENTS SUBMITTED

1. D.P. Holmes, J.S. Hochgraf, M. Libuit. “Active Shear Thickening Fluid Composite Orthosis,” 2012.
2. H.A. Stone, D.P. Holmes, G. Froehlicher. “Control and Manipulation of Fluid Flow via Elastic Deformations,” 2011.
3. R.M. Martinez and G.M. Whitesides, “Programmable Paper-Elastomer Composites as Pneumatic Actuators,” PROV Priority, 2012.
4. R.M. Martinez and G.M. Whitesides, “Apparatus, Systems, and Method for Providing Fabric Elastomer Composites as Pneumatic Actuators,” PCT, 2013.
5. J.-Y. Sun, X. Zhao, W.R.K. Illeperuma, K.H. Oh, D.J. Mooney, J.J. Vlassak, Z. Suo, “Interpenetrating networks with covalent and ionic crosslinks for extremely stretchable and tough hydrogels,” 2012.
6. J. Aizenberg and P. Kim, “Hierarchical Structured Surfaces To Control Wetting Characteristics” *PCT/US11/44553* **2011**.

PATENTS AWARDED

None during report period.

INNOVATIVE DESIGN AND PROCESSING OF MULTI-FUNCTIONAL ADAPTIVE STRUCTURAL MATERIALS
GRANT NUMBER: W911NF-09-1-0476

Principal investigator(s), affiliation

SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS

Our project on adaptive structural materials begins with bone as a source of inspiration for adaptive materials systems. Examining the structure of natural bone leads to the five guiding principles for our research: (i) load bearing by hierarchically porous materials; (ii) adaptive, sensing load and supplying mass to reinforce at load-bearing sites through material deposition and dissolution; (iii) transport of materials using fluid flow through low density porous systems; (iv) energy to drive processes taken from storage sites, which are replenished by internal or external energy generation; (v) mechanisms, which are not fully understood for bone, but knowing the fundamental mechanisms allows these to be adjusted for application to synthetic systems. The principal problem addressed by the program was how to change soft materials into hard structures reversibly, in response to load or other environmental stresses. The approaches used (Fig. 1) included (i) reversible jamming, layering, welding and/or percolation; (ii) dissipative materials; and (iii) granular chemistry.

ELECTROCHEMICAL WELDING AND DEWELDING

Electroplating on Compliant Substrates

Ilhan A. Aksay, Princeton University

Measuring the dissolution dynamics of thin films in situ both with spatial and temporal resolution can be a challenging task. Available methods such as scanning electrochemical microscopy rely on scanning the specimen and are intrinsically slow. We developed a characterization technique employing only an optical microscope, a digital charge coupled device camera, and a computer for image processing. It is capable of detecting dissolution rates of the order of nm/min and has a spatial and temporal resolution which is limited by the imaging and recording setup. We demonstrate the capabilities of our method by analyzing the electrochemical dissolution of copper thin films on gold substrates in a mild hydrochloric acid solution (Fig. 1a). Due to its simplicity, our technique can be implemented in any laboratory and can be applied to a variety of systems such as thin film sensors or passive coatings.[1]

Electrowelding

George M. Whitesides, Harvard University; Ilhan A. Aksay, Princeton University

Thermal welding is a powerful technique for joining metal components; however, it has materials limitations and it is not reversible. For example, steel is easily welded together using thermal welding, but non-conductive components, like plastics, and non-metallic components, like

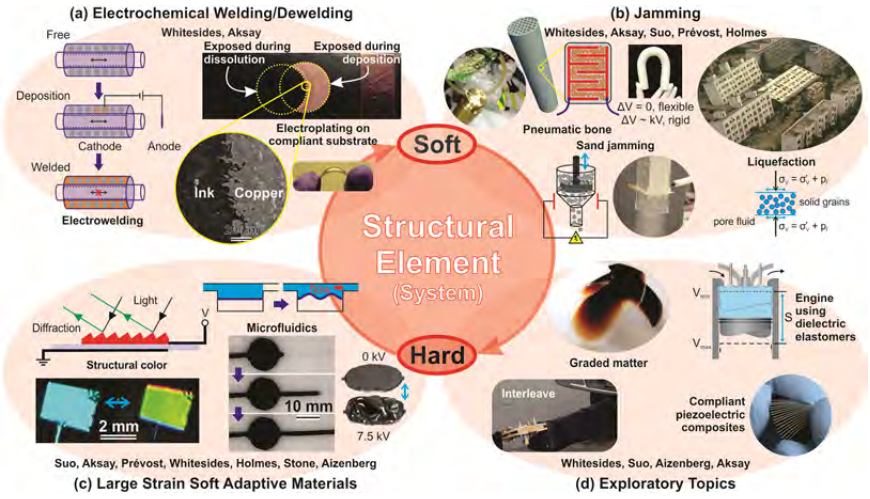

Figure 1: Reversible soft to hard transition and approaches.

carbon fiber, cannot be joined using thermal welding, and a thermal weld is designed for permanence. We desire a method that can reversibly deposit metals onto metals and non-conductive materials, at low temperatures, for the purpose of creating structural connections.

Our strategy exploits the versatility of electrochemistry to reversibly join a variety of different materials though electrowelding (Fig. 2a). Experimentally we have designed structures and systems that maximize mass transport and adhesion. One of the key principles in the experimental design is the concept of amplification—a small amount of material deposited can make a large difference in the structures properties.

The system we have primarily worked with consists of two interpenetrating nickel mesh cylinders (Fig. 2b). Mesh is chosen to allow free mass transport through the system. The mesh cylinders are separated by steel rods and a sacrificial zinc anode is inserted into the center of the inner cylinder. The assembly is placed into a deposition bath containing zinc chloride and a constant current of 1 A is applied between the zinc anode and the outer mesh cylinder welding the pieces together with zinc (Fig. 2c). The welded assembly, created under these conditions, could withstand a shear stress of 2 kPa; depositing more metal and optimizing adhesion improves results. The zinc weld was reversed by switching the position of the counter electrode (Fig. 2b) and applying a constant potential of 1V.

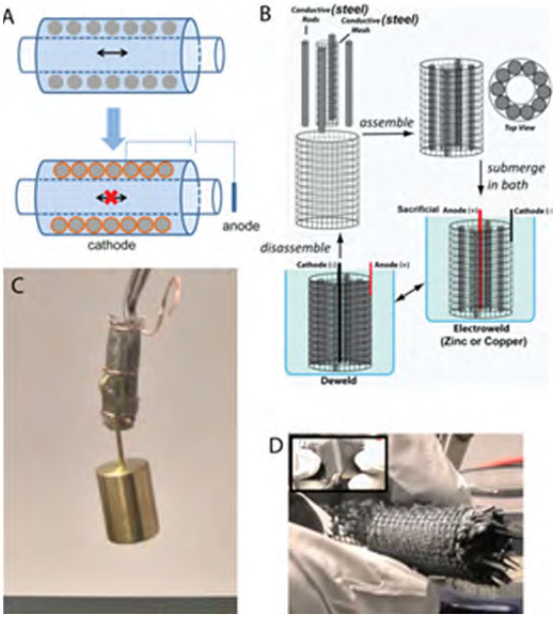

Figure 2. (a) Schematic of electrowelding process joining two cylinders. (b) Experimental design for zinc electrowelding. (c) A zinc electroweld under 2 kPa of sheer stress. The inner mesh cylinder is being held and stress applied between inner and outer cylinders. (d) Carbon fiber fabric electrowelded with zinc to an insulated steel mesh. Inset is the carbon fabric before welding.

Zinc electrowelding is not limited to conductive nickel mesh and steel rods. We were able to weld together steel mesh (coated with and insulating material) to a conductive carbon mesh following conditions similar to those above. Again this process was completely reversible.

Electrochemistry of Graphene

Ilhan A. Aksay, Princeton University

Capacitance of Functionalized Graphene Sheets

We present a general method for characterizing the intrinsic electrochemical properties of graphene sheets, such as the specific double-layer capacitance, in the absence of porosity-related artifacts and uncertainties. By assembling densely tiled monolayers of electrically insulating or conductive functionalized graphene sheets (FGSs) onto electrode substrates (gold and highly oriented pyrolytic graphite), we demonstrate our ability to isolate their intrinsic electrochemical response in terms of surface-specific double-layer capacitance and redox behavior. Using this system, the electrochemical properties of various types of graphene can be directly compared without the need to take into account changes in electrode morphology and electrolyte accessibility arising because of varying material properties.[2]

Graphene-Ionic Liquid Capacitors

Colloidal dispersions of graphene oxide in a water-ionic liquid solution are used to co-

assemble graphene-ionic liquid laminated structures by first evaporating the water component of the dispersion medium and then thermally reducing the graphene oxide to an electrically conducting functionalized graphene state. This process yields a graphene-based electrode in which the ionic liquid serves not only as the working electrolyte but also as a spacer to separate the functionalized graphene sheets and to increase the electrolyte-accessible surface area. By optimizing the amount of ionic liquid and the degree of graphene oxide reduction, mass-specific capacitances up to 154 F/g of graphene were achieved at a discharge current of 0.2 A/g. At a low ionic liquid content of 60 wt%, one of the highest volume-specific capacitances of approximately 61 F/cm^3 was attained. Tuning the degree of thermal reduction of the graphene oxide and increasing the ionic liquid content to 86 wt% lead to equally high mass-specific capacitance but showed improved capacitance at high charge/discharge rates, maintaining 90% of its value at 500 mV/s. This bottom-up approach to electrode design is simple, scalable, and ideally suited for combining potentially any graphene-based material with any ionic liquid electrolyte.[3]

FGS Conductivity

We studied the local voltage drop in functionalized graphene sheets of sub-μm size under external bias conditions by Kelvin probe force microscopy. Using this noninvasive experimental approach, we measured ohmic current voltage characteristics and an intrinsic conductivity of about 3.7×10^5 S/m corresponding to a sheet resistance of 2.7 kΩ/sq under ambient conditions for graphene produced via thermal reduction of graphite oxide. The contact resistivity between functionalized graphene and metal electrode was found to be $<6.3 \times 10^{-7}$ Ωcm^2.[4]

Electrochemical Performance of FGS

Graphene-based electrodes have recently gained popularity due to their superior electrochemical properties. However, the exact mechanisms of electrochemical activity are not yet understood. Here, we present data from NADH oxidation and ferri/ferrocyanide redox probe experiments to demonstrate that both (i) the porosity of the graphene electrodes, as effected by the packing morphology, and (ii) the functional group and the lattice defect concentration play a significant role on their electrochemical performance.[5]

JAMMING

Granular Materials

George M. Whitesides, Harvard University; Ilhan A. Aksay, Princeton University

Solid granular materials undergo a discrete transition from a soft phase to a hard phase when the granule density, or pressure, is increased beyond a certain point such that the granules become jammed together. This jamming phase transition can be used to reversibly switch between hard and soft states of a material with little energy expenditure, yielding materials with adaptive mechanical properties. We are investigating the effects of electromagnetic interactions and granule anisotropy on the mechanical properties of the jammed vs. unjammed states. Recent work in this field has focused exclusively on using coffee grounds and other homogeneous fine granular matter as a jamming material for switchable material stiffness. We have found that external electric fields as well as granule charge, heterogeneity, and geometry can have significant effects on the soft/hard transition from the unjammed to the jammed state. To this end, we have developed four primary test systems to explore the jamming transition:

Galvanic Microreactor

We report on a technique that utilizes an array of galvanic microreactors to guide the assembly of two-dimensional colloidal crystals with spatial and orientational order. Our system is com-

prised of an array of copper and gold electrodes in a coplanar arrangement, immersed in a dilute hydrochloric acid solution in which colloidal micro-spheres of polystyrene are suspended. Under optimized conditions, two-dimensional colloidal crystals form at the anodic copper with patterns and crystal orientation governed by the electrode geometry. After the aggregation process, the colloidal particles are cemented to the substrate by co-deposition of reaction products. As we vary the electrode geometry, the dissolution rate of the copper electrodes is altered. This way, we control the colloidal motion as well as the degree of reaction product formation. We show that particle motion is governed by a combination of electrokinetic effects acting directly on the colloidal particles and bulk electrolyte flow generated at the copper-gold interface.[6]

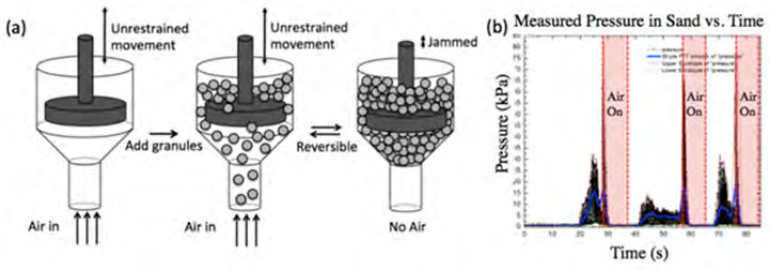

Figure 3. Jammed piston.

Jammed Piston

We study the use of airflow for controlled reversibility of the jamming transition (Fig 3a). A piston in a tube is free to move when no granular media is present. Introducing airflow into the tube prevents granular material from jamming and does not impede the movement of the piston motion. With no airflow, the media is compressed into the jammed state, significantly raising the pressure. We measure the reversible transition into and out of the jammed state of sand (Fig. 3b).

Electric Mesh

We investigate the effect of electric fields and granular charging on the jamming transition. A high voltage is applied between a conducting mesh, embedded in a vertical column of sand, and a ground plane (Fig. 4a). We find that application of V=-50kV can reversibly stop the flow of sand through the column (Fig. 4b,c). We are currently investigating whether dielectric forces or granular charging are the primary causes of jamming in this system.

Charged Beads

We study the effects of granular charging on the phase transition of a jammed crystal. Beads of opposite electron affinity (Delrin/Teflon), contained in a vibrating dish, will self-assemble into a jammed crystal structure (Fig. 5).

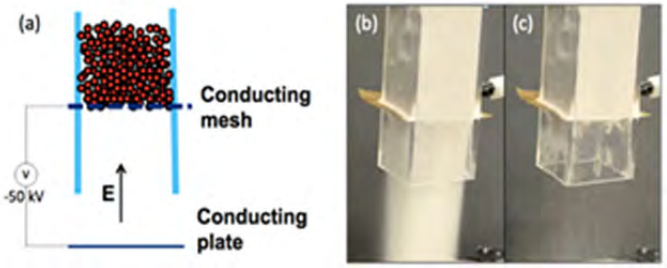

Figure 4. (a) Schematic of sand-based jamming system using a conducting mesh. (b) V = 0 kV. (c) V = -50 kV.

Structural Beams

We investigate the effect of granular geometry on the reversible load bearing capabilities of the jammed state. We believe that rod-like jamming materials can give long-range rigidity (Fig 6a) and tetrapods can be used to help lock granules together. We use a 3-point flexural test to study the load bearing capability of a hollow flexible tube filled with different granular particles

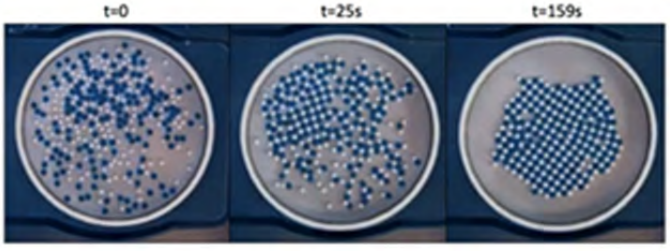

Figure 5. Charged beads self-assembling into a crystal.

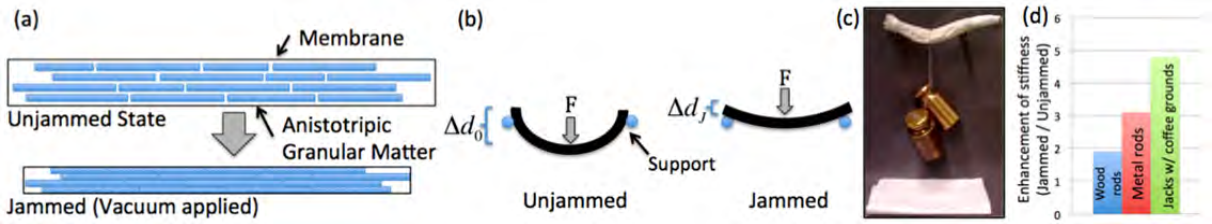

Figure 6. Reversible load-bearing of a composite beam subjected to evacuation to jam granular materials.

(Fig. 6b). When vacuum is applied to the beam, the granules jam and the beam becomes rigid; evacuating the beam makes it flexible again. We have found that a 2cm x 20cm beam filled with 1" metal rods can support 4 kg (Fig 6c): when the beam pressure is reverted to atmosphere, the beam folds and collapses. Finally, we have measured the stiffness enhancement of various granular materials (1" wooden rods, 1" metal rods, and metal jacks with coffee grounds), shown in Fig. 6d.

LARGE STRAIN SOFT ADAPTIVE MATERIALS

Dielectric elastomers with giant voltage-induced deformation

Zhigang Suo, Harvard University

A membrane of a dielectric elastomer deforms when a voltage is applied through its thickness. The achievable voltage-induced deformation is strongly affected by how mechanical loads are applied. We have shown that a relatively simple setup—a clamped membrane of dielectric elastomer—can achieve Giant voltage-induced stretch of 3.6.[7] This setup also displays remarkably rich interplay of nonlinear processes, including local instability, wrinkling, and snap-through instability. Snap-through instability itself does not always lead to failure; under certain conditions a membrane can survive the snap and reach a stable state.

Large voltage-induced deformation has been demonstrated for a membrane under equal-biaxial forces, but only small voltage-induced deformation has been observed for a membrane under a uniaxial force. We interpret this difference theoretically.[8] Our theory also predicts that, when the deformation of a membrane is constrained in one direction, a voltage applied through the thickness of the membrane can cause it to deform substantially in the other direction. Experiments are performed on membranes under equal-biaxial forces and uniaxial forces, as well as on fiber-constrained membranes of two types: a dielectric elastomer membrane with carbon fibers on both faces, and two dielectric elastomer membranes sandwiching nylon fibers.[8] Experiments with membranes under uniaxial forces capture the theoretical prediction that the maximum actuation decreases when the applied force increases. Experiments with fiber-constrained membranes give voltage-induced unidirectional strains up to 28%.

Dielectric Elastomer Actuators with Elastomeric Electrodes

Zhigang Suo, Harvard University

For many applications of dielectric elastomer actuators, it is desirable to replace the carbon-grease electrodes with stretchable, solid-state electrodes. We attach thin layers of a conducting silicone elastomer to prestrained films of an acrylic dielectric elastomer and achieve voltage-actuated areal strains over 70%.[9] The influence of the stiffness of the electrodes and the prestrain of the dielectric films is studied experimentally and theoretically. It is demonstrated that actuators with fully compliant and those with solid electrodes show qualitatively the same response to applied voltages. While the actuation amplitudes are reduced with solid electrodes, we still observe a transition from electromechanically unstable to stable characteristics which allows for large actuation amplitudes. Although the actuator performance is impeded by the presence of sol-

id electrodes, their use offers advantages as well, such as structural stability, compatibility with more complex polymer systems, or the potential for frameless actuator designs. Solid electrodes therefore constitute a viable alternative to fully compliant but otherwise more limited electrode designs.

Tough gel

Zhigang Suo, Harvard University

Hydrogels are used as scaffolds for tissue engineering, vehicles for drug delivery, actuators for optics and fluidics, and model extracellular matrices for biological studies. The scope of applications, however, is often severely limited by the mechanical behavior of hydrogels. Most hydrogels are brittle, having fracture energy on the order of 10 J/m2. We report hydrogels made of polymers forming networks via ionic and covalent crosslinks.[10] Although such a gel contains ~ 90% water, it can be stretched beyond 20 times its initial length, and has fracture energy of ~9000 J/m2. Even for samples containing notches, a stretch of 17 is demonstrated. The toughness is attributed to the synergy of two mechanisms: crack bridging by the network of covalent crosslinks, and hysteresis by unzipping the network of ionic crosslinks. Furthermore, the network of covalent crosslinks preserves the memory of the initial state, so that much of the large deformation is removed upon unloading. The unzipped ionic crosslinks cause internal damage, which heals by re-zipping. These gels may serve as model systems to explore mechanisms of deformation and energy dissipation. Hydrogels with enhanced mechanical properties will expand the scope of their applications.

Thermoporoelastic response of a fluid-saturated porous sphere

Jean-Herve Prevost, Princeton University

The fully coupled thermo/hydro/mechanical response of a fluid saturated porous sphere subject to a pressure stress pulse on the outer boundary is considered. A full analytical method is developed and an exact unique solution of the coupled equations is presented. This generality allows us to simulate a variety of practical problems.[11]

Control and manipulation of flow due to elastic deformation

Howard Stone, Princeton University; Douglas P. Holmes, Virginia Tech

Controlling and directing the flow within a microfluidic device or channel is important for a variety of applications ranging from self-healing devices to microfluidic diagnosis and analysis. Significant advances in microfluidic accuracy have been made using externally actuated valves, though the presence of external power and hardware lead limit the devices range of use. Developing a fully internally controlled device will allow the technology to be used as highly portable or embeddable tool for directing fluid flow, such as for controlling localized flow in adaptable materials. For example, in the advance we describe here we have designed and implemented a method for directing fluid flow in deformable materials such that the flow is from regions of low to high stress, which is consistent with a necessary step if material is to be directed internal to a device for reinforcement where stresses are large.

We have demonstrated significant steps towards this goal. In particular, we utilize elastic deformations within a flexible device via mechanical actuation to control and direct fluid flow. A flexible arch within a micro- or milli-fluidic channel is designed to prevent fluid flow in its initial, strain-free state, while upon stretching or bending the device, the arch deformable arch acts like a valve allowing fluid to flow. A demonstration is given in Fig. 7a and the design principle is sketched in Fig. 7b. Red denotes liquid, which resides in a pressurized chamber and so flows when the valve opens.

The design features take advantage of soft lithography. A PDMS substrate with a channel of

length L is uniaxially stretched to length ΔL in the direction orthogonal to the channel. A thin PDMS film, with thickness h =O(100 μm), is bonded to the stretched PDMS substrate, and upon release of the uniaxial strain buckles to form an arch of height w along the length of the channel. If we consider the symmetric buckling of a bar, i.e. the one- dimensional Euler column, we can describe the deformation quantitatively. Experimental measurements and predictions are shown in Fig. 8 and demonstrate our ability to predict and control the deflection of the film.

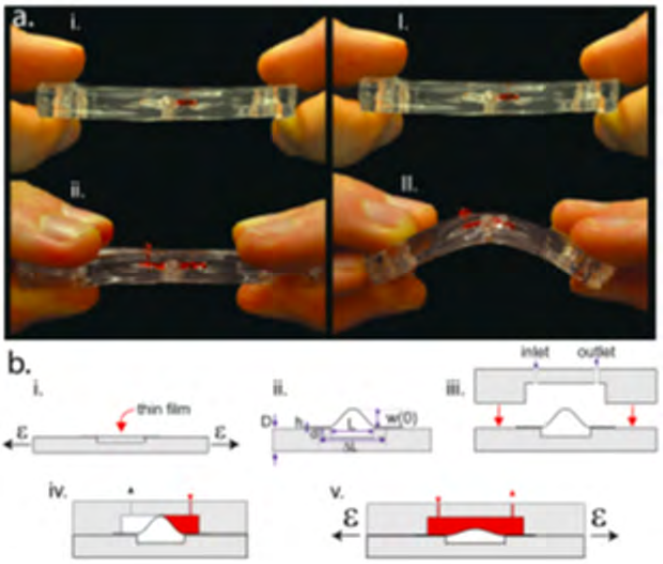

Figure 7. (a) *i* and *I* Images of a flexible microfluidic device in its initial state containing a fluid (red) that cannot flow. As the material is *ii* stretched or *II* bent, the flexible valve within the device deforms to allow fluid to flow. (b) A schematic illustrating the fabrication of the device. *i*. The substrate is stretched and a thin film is bonded to it. *ii*. Upon relaxation of strain, the thin film buckles to an arch. *iii*. The top layer of the device is bonded to the bottom layer, with the arch acting as a flexible valve. *iv*. After fabrication, fluid is unable to flow within the microfluidic channel. *v*. Upon stretching, or bending, the thin elastic arch within the channel deforms allowing fluid to flow.

In the next step a channel is placed above this design, and this film is used as a valve. The channel is connected to a liquid-filled reservoir, which is pressurized. We have measured the flow rate through the channel for different "valve" deflections. In addition, we have theoretically calculated the flow rate for different deflections of the valve using an extension of lubrication theory. The results are summarized in Fig. 9, which compares theory and experiments. In this way, we have quantified everything about the valve, from its elastic deformation as a function of an applied strain, to the flow rate through the partially blocked channel.

Dynamic responses of soft materials – Bending, buckling and twisting

Howard Stone, Princeton University; Douglas P. Holmes, Virginia Tech

Soft materials (e.g. tissue, gels) undergo volume changes and instabilities when subjected to external stimuli. Such reconfigurable materials offer significant possibilities for novel adaptable materials. We provide two examples in this section. In particular, we present the dynamic instabilities that occur by straining an elastomer anisotropically. We have shown how thin elastic plates, both narrow beams and circular disks, can undergo rapid bending and buckling instabilities after exposure of the cross-linked, elastic network to a favorable solvent that causes swelling. The equilibrium shape of the swollen material is determined by the minimization of the system's bending energy in conjunction with any exter-

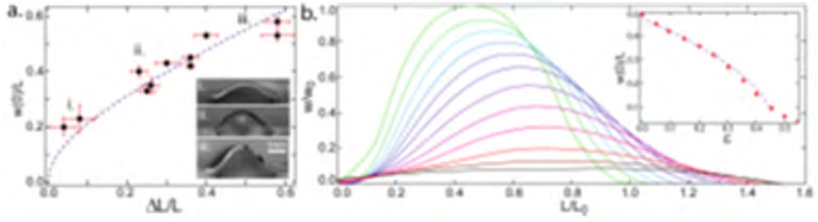

Figure 8. (a) Normalized deflection of the center of the arch w(0) is plotted as a function of the strain with experimental points obtained by image analysis. *i*, *ii* and *iii* are example images from different stretches ΔL. The analytical curve is determined by the buckling of an Euler column. (b) Profiles of the buckled thin film after fabrication. The lines correspond to the experimentally measured contour via image analysis. As the device is uniaxially stretched from L = L_0 = 1, i.e. the initial state after fabrication described in (a), to a new length the contour of the film goes from buckled to flat. The inset shows the height of arch at its center as a function of uniaxial extension. The dashed line corresponds to the theoretically predicted curve.

nal forces and constraints; we focus on dynamics. We have developed a quantitative understanding of this phenomenon using theoretical ideas of poroelasticity to illustrate shape changes possible for applications involving adaptable materials.

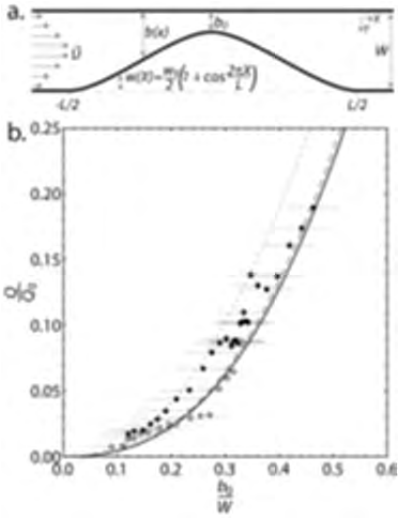

Figure 9. (a) A schematic of fluid flow within the microfluidic device. A fluid with velocity U flows from left to right over an elastic arch whose shape w(X). The height of the gap is described by the compliment of the arch's height, b(X), than spans a channel height W. (b) The flow rate Q normalized by the two-dimensional flow in a rectangular channel Q0 and plotted versus b0=W. The dotted line is the zeroth order solution to the lubrication theory, while the dashed and solid lines represent the second and fourth order solutions, respectively. Excellent agreement between theory and experiment is obtained.

Controlled bending of a beam driven by swelling caused by solvent imbibition

We deposit a small drop of a favorable solvent (typically hexane or a silicone oil) on a porous gel (e.g. PDMS). Upon absorption of the liquid, the gel swells and shape changes follow as illustrated in Fig. 10 for various shapes of beams. In particular, an unconstrained beam bends along its length, while a circular disc bends and buckles with multiple curvatures that rotate azimuthally around the disc (Fig. 10,12). Theoretical interpretations motivated by the complementary thermal expansion problem of transient shape changes triggered by time-dependent heating, when combined with the theoretical ideas of poroelasticity, offer both experimental and quantitative theoretical interpretations. In the simplest case of an initially straight beam (Fig. 10a), the swelling first induces bending of the beam into a simply curved state. As the liquid penetrates the gel and swells it uniformly, then the beam recovers its initial straight state. If the beam has an initially curved state, the swelling can produce a "snap buckle" to a state with opposite curvature (Fig. 10b,c).

We have quantified the dynamics by measuring, for the configuration in Fig. 10a, the curvature of the beam at its center (Fig. 11). The curvature begins equal to zero (the flat state), bends to its most curved state at a time τ_{min}, and then returns to the flat state. The curvature at the center is reported as a function of time in Fig. 11b (several beams and several different viscosity liquids are used) and displayed in dimensionless terms (obtained from theory) in Fig. 11c. The theory collapses data for different beams and different viscosity liquids (Fig. 11d).

Bending of a circular disk driven by swelling caused by imbibition of a solvent

The same type of solvent-induced swelling for a circular disc causes bending and buckling; deformation modes travel as waves that rotate azimuthally around the disc (Fig. 12).[12] A plot of curvature versus time illustrates that the disc's principle curvatures are equal at short times. Once a bifurcation point is reached, one curvature increases while the other decreases until the disc relaxes back to its original shape. Since there is no equilibrium direction for the principle curvatures, the buckle rotates as a wave-like motion azimuthally around the disc (Fig. 12).

Electrically driven motion of dielectric liquids

Howard Stone, Princeton University; Douglas P. Holmes, Virginia Tech

In electrohydrodynamic (EHD) pumping, fluid forces are generated by the interaction of electric fields with the charges they induce in the fluid. In particular, when a potential difference is imposed on a layer of dielectric liquid between two electrodes, an electrical shear stress acts on the interface of the liquid and drives a fluid flow. Here, we demonstrate the effect of the tangential electric field on the motion of dielectric liquid in a narrow wedge-shaped gap and show the

ability to selectively move liquids in narrow columns from a reservoir (Fig. 13). We believe that such mechanisms, coupled with other ideas in the MURI for controlling electrical potential, offer opportunities for internally moving liquid in a porous structure.

The fluid is driven to high electrical potential region due to tangential field, while if the local field gets too high the liquid interface takes a conical shape (Taylor cone) induced by a normal electric field to the interface, which leads to an instability. We have performed a large number of experiments varying the fluid viscosity and gap geometry. The dynamics are controlled by the viscously dominated motion of the liquid film and we have published this work in the past few months.[13]

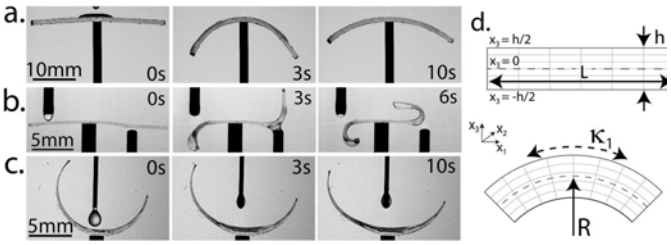

Figure 10: Global and localized bending of beams swollen non-homogenously with a favorable solvent. (a) A narrow beam with free edges is swollen non-homogenously by placing a droplet of hexane on one side. The expansion of the top surface of the beam causes the material to initially bend sharply and then relax back to its initial shape. (b) A beam swollen with hexane at two locations on opposite faces leads to localized bending of opposite curvatures. (c) An initially curved beam bends and decreases its curvature when swollen with a favorable solvent.

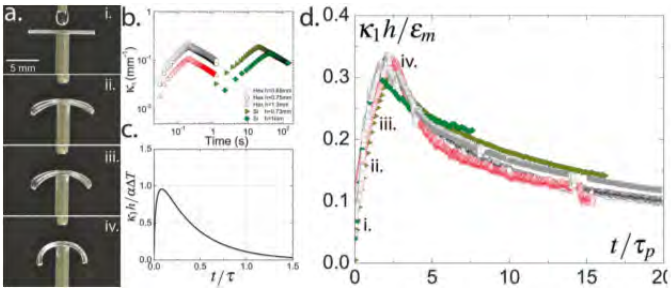

Figure 11: Dynamics of beam bending. (a) Images of a beam swollen with silicone oil bending to its maximum curvature. (b) Raw data of curvature versus time for beams of various thicknesses swollen with different solvents. (c) A plot of normalized beam curvature (κ) versus time normalized by the diffusion time based on the analogy with the thermal bending of beams. (d) The raw data from b is normalized based on the parameters in the theory we developed, with time scaled by the poroelastic time, τ_p. The data for a range of beam thicknesses and fluid properties collapses to a qualitatively similar profile that is predicted by the theory (see Holmes et al. 2011).

Structural Color

Ilhan A. Aksay, Princeton University

We have developed electrically conducting silicone elastomer nanocomposites that serve both as compliant electrodes in an electrostatic actuator and, at the same time, as optically active elements creating structural color. We demonstrate the capabilities of our setup by actuating an elastomeric diffraction grating and colloidal-crystal-based photonic structures (Fig. 1c).[14]

Buckling-induced reversible symmetry breaking and chiral amplification in supported cellular structures

Joanna Aizenberg, Harvard University

Chirality on all length scales is crucial in understanding and controlling the behavior of living and non-living systems because the presence or absence of chirality in the structures plays important roles in their interactions with molecules, enzymes, light, and mechanical stress. While at the molecular scale few systems have been reported capable of spontaneous symmetry breaking followed by amplification of this initial bias to molecules of single handedness, the generalization of this process to larger

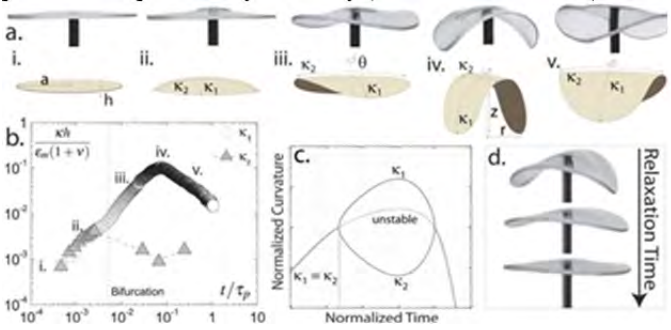

Figure 12: Bending and bifurcation of circular discs. (a) Optical images and schematic as a circular disc buckles axisymetrically, i.e. the two curvatures are equal, before bifurcating with distinct curvatures κ_1 different than κ_2. (b) A plot of normalized curvature versus time. A bifurcation occurs causing the two curvatures to differ in magnitude (dashed line added to guide the eye). (c) Normalized curvature versus normalized time is determined by minimizing the total strain energy of the disc. Our experimental data is in very good agreement with this theory. (d) Images of the circular disc as it relaxes back to its initial, flat state.

length scales remains a fundamental challenge. We demonstrate chiral symmetry breaking followed by full amplification to yield uniform chiral patterns of single handedness utilizing buckling, which is traditionally considered a failure mode.

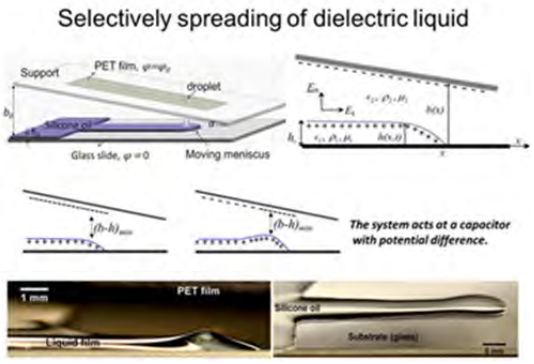

Figure 13

Guided by extensive theoretical analysis, we tailored model cellular structures where buckling induces a reversible switching between achiral and chiral configurations. Given that the proposed mechanism is governed by a mechanical instability that is scale-independent, the principle can be generalized over a wide range of length scales, geometries, materials, and stimuli as shown in Fig. 14. Importantly, this scale-independent behavior allows us to scrutinize the kinetic processes of both the nucleation which causes the symmetry breaking, and the subsequent propagation/cascade of this chirality which is assisted by a localized self-correction mechanism to yield uniform patterns of single handedness. Furthermore, we show that the sign of chirality can be encrypted, read out and overwritten in the architecture as demonstrated in Fig. 15. Buckling- induced chiral pattern formation therefore introduces a versatile class of transformable architectures with potential practical applications ranging from switchable optics to tunable mechanical metamaterials.

Enriching libraries of mechanically robust high-aspect-ratio micro- or nanostructures by rapid, low-cost, benchtop nanofabrication method: Structural Transformation by Electrodeposition on Patterned Substrates (STEPS)

Joanna Aizenberg and George M. Whitesides, Harvard University

We developed a protocol for transforming the structure of an array of high-aspect-ratio (HAR) micro/nanostructures into various new mechanically reinforced geometries based on STEPS fabrication method reported last year. Polymeric HAR arrays are soft lithographically replicated from a Bosch etched silicon master pattern. A set of metal electrodes is patterned on the original pattern using various conditions to which conductive polymers are electrodeposited transforming the original structure into a wide range of user-defined new designs including scaled replicas with sub 100 nm-level control of feature sizes and complex 3D shapes such as tapered or bent columnar structures bearing hierarchical features. Fig. 16 shows a library of such modified micro/nanostructures that can be created by STEPS fabrication method. Gradients of patterns and shapes on a single substrate can also be produced. This bench-top fabrication protocol allows the production of customized libraries of arrays of closed-cell or isolated HAR micro/nanostructures at a very low cost within a week when starting from a silicon master that other-

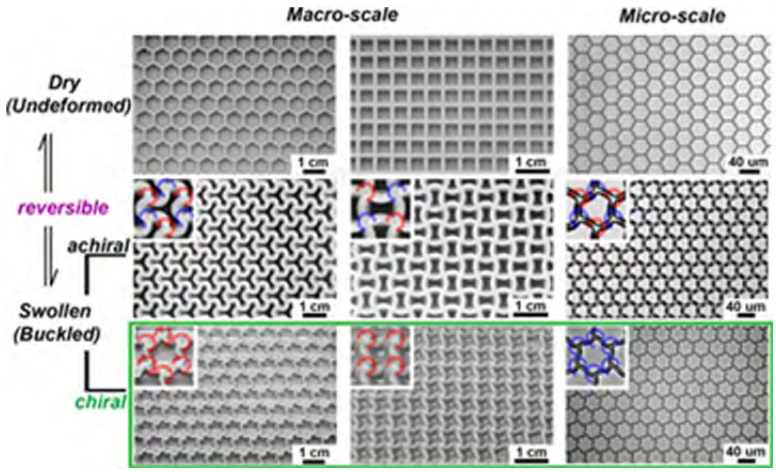

Figure 14. Demonstration of reversible achiral and chiral pattern formation by swelling. The color-coded arrows in the insets indicate the handedness of vertices.

wise would be very expensive and slow to produce using conventional MEMS techniques. Fig. 17 highlights the capability and usefulness of STEPS fabrication method that were featured as the cover story of each issue of *Nano Letters* and *Nature Protocols* (February 2012).

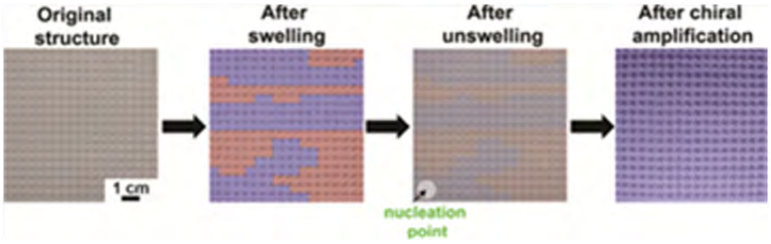

Figure 15. Visualization of chiral amplification. Rapid swelling of original structures gives a statistically equal distribution of left- and right-handed structures. These chiral domains can be selected and amplified. We first map the chiral domains upon rapid swelling. Subsequently, the structure recovers the unbuckled configuration, where the handedness map is given in faded red and blue. Buckling is then initiated at a location selected from the handedness map to induce a uniform pattern of the desired handedness.

Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity

Joanna Aizenberg, Harvard University

Creating a robust synthetic surface that repels various liquids would have broad technological applications for areas ranging from biomedical devices and fuel transport to architecture but has proved extremely challenging. Inspirations from natural nonwetting structures, particularly the leaves of the lotus, have led to the development of liquid-repellent microtextured surfaces that rely on the formation of a stable air–liquid interface. Despite over a decade of intense research, these surfaces are, however, still plagued with problems that restrict their practical applications: limited oleophobicity with high contact angle hysteresis, failure under pressure and upon physical damage, inability to self-heal and high production cost. To address these challenges, we have developed a strategy to create self-healing, slippery liquid-infused porous surface(s) (SLIPS) with exceptional liquid- and ice-repellency, pressure stability and enhanced optical transparency.

Our approach—inspired by *Nepenthes* pitcher plants—is conceptually different from the lotus effect, because we use nano/microstructured substrates to lock in place the infused lubricating fluid (Fig. 18). We define the requirements for which the lubricant forms a stable, defect-free and inert 'slippery' interface. This surface outperforms its natural counterparts and state-of-the-art synthetic liquid-repellent surfaces in its capability to repel various simple and complex liquids (water, hydrocarbons, crude oil and blood), maintain low contact angle hysteresis (<2.5º), quickly restore liquid-repellency after physical damage (within 0.1–1 s) (Fig. 19), resist ice adhesion, and function at high pressures (up to about 680 atm). We show that these properties are insensitive to the precise geometry of the underlying substrate, making our approach applicable to various inex-

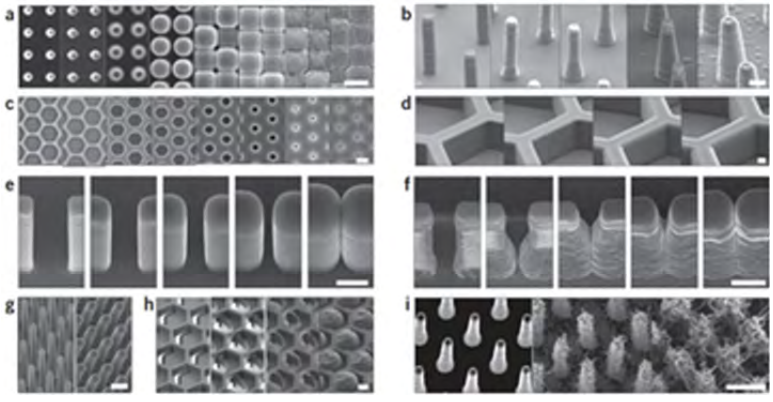

Figure 16. Example SEM images of STEPS-modified structures. (a) STEPS-I on a nanopost array, modifying the diameter and the gap. (b) STEPS-II on a micropost array, converting posts into cones. (c) STEPS-I on a honeycomb microwell array, reducing the well size and increasing the wall thickness. (d) STEPS-II on honeycomb microwell array with gradually increasing overhanging features with re-entrant curvature. (e, f) Comparison of STEPS-I and STEPS-II methods to fill a gap between adjacent HAR features, side-by-side filling when STEPS-I method is used (e) or bottom-to-top filling when STEPS-II method is used (f). (g) STEPS-III on a nanopost array, converting posts into bent posts. (h) STEPS-III on a honeycomb microwell array, creating anisotropically grown polymer lips, pockets and hollow dumplings. (i) STEPS-IV on nanopost array, converting the structure into hierarchical structures. Scale bars, 2 μm (a–g, i) and 10 μm (h), respectively.

pensive, low-surface-energy structured materials (such as porous Teflon membrane). We envision that these slippery surfaces will be useful in fluid handling and transportation, optical sensing, medicine, and as self-cleaning and antifouling materials operating in extreme environments.

Exploratory Topics

George M. Whitesides, Harvard University; Ilhan A. Aksay, Princeton University

In addition to major thrusts in electrowelding and jamming, we examined topics that fit into our overall program vision and would lead to possible new research areas.

Van der Waal bonding of fiber reinforced sheets

We created a series of atomically smooth, fiber reinforced elastomeric sheets (Fig. 20a). When stacked, the conformal contact between the sheets leads to strong Van der Waal interactions and the assembly can withstand very high tensile loads (Fig. 20a, b). Our main interests concerned the transfer of shear forces through the elastomer to the sheets, combinations of different fibers, and if this approach could be combined with electrowelding or dielectric elastomers using conductive carbon fabrics as reinforcers.

2D Jamming surfaces

We investigated the jamming of hard materials on two dimensional (2D) surfaces. The experimental design (Fig. 21a) relied on high aspect ratio pillars arranged sparsely on stretchable elastomeric surfaces. By collapsing the surface using vacuum we could consolidate the hard objects at will (Fig. 21b, c). This strategy can be used to reversibly change the mechanical, optical, or electric properties of a surface.

1D Jamming surfaces

Similar to the two dimensional system, we also investigated jamming of one dimensional systems (1D) (Fig. 21d, e). This system can be useful for adapting resistance to orthogonal forces and torque.

Pneumatic bone

We examined hierarchical pneumatic structures to amplify stiffness via pneumatic pressurization. The current design (Fig. 22) can support a load of 2 kg at

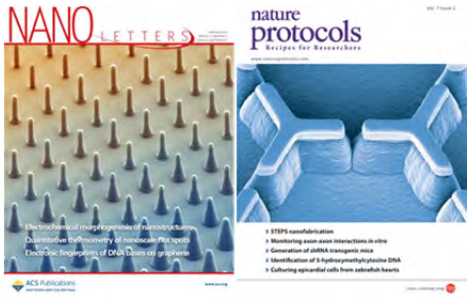

Figure 17. Two recent journal cover images (both were published in February 2012) highlighting the unique capability of STEPS fabrication method and representative mechanically reinforced micro/nanostructures. Left: A combined SEM images of nanoposts showing how the structure is transformed to reinforced cone shapes by a series of electrochemical deposition. Right: An SEM image showing an array of 'Y' shape microstructure with reinforced bottom.

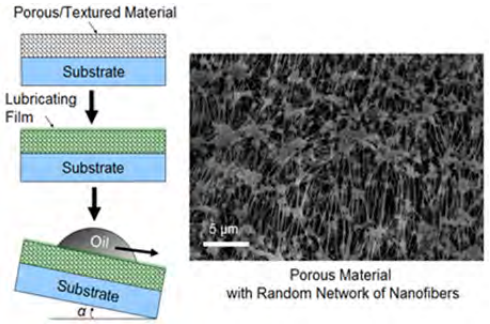

Figure 18. (Left) Schematics showing the fabrication of a slippery surface by infiltrating a functionalized porous solid with a low-surface energy, chemically inert liquid to form a physically smooth and chemically homogeneous lubricating film on the surface of the substrate. (Right) A scanning electron micrograph showing the morphologies of a Teflon-based porous nanofiber network.

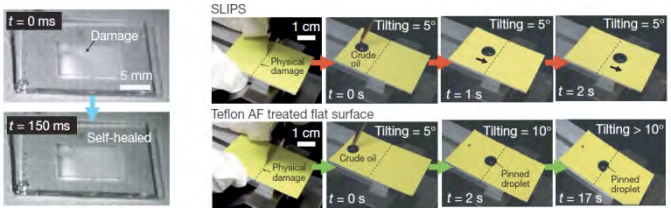

Figure 19. (Left) Time-lapse images showing the capability of a SLIPS to self-heal from physical damage ~50 mm wide on a timescale of the order of 100 ms. (Right) Time-lapse images showing the restoration of liquid repellency of a SLIPS after physical damage, as compared to a typical hydrophobic flat surface (coated with DuPont Teflon AF amorphous fluoropolymers) on which oil remains pinned at the damage site.

650 mBar. Other device architectures and new elastomer/fiber composites that were developed to increase the stiffness amplification.

Graded Matter

Inspired by the beaks of squid and octopi, we were interested in creating structures with stiffness gradients. We wanted to be able to not only create the gradients simply; we wanted to be able to reconfigure or reverse the gradients in an equally simple way. Our approach was to embed ferromagnetic enforcing powder (iron) inside of a PVA-copolymer (a thermoplastic) matrix. By heating the thermoplastic matrix in the presence of a magnetic field we could easily create a gradient of enforcing powder (Fig. 23a). We sectioned and measured the compressive moduli of these structures to quantify the gradients (Figure 23b).

High Surface Area Electroactive Films

We described a scalable method for producing continuous graphene networks by tape casting surfactant-stabilized aqueous suspensions of functionalized graphene sheets. Similar to all other highly connected graphene-containing networks, the degree of overlap between the sheets controls the tapes' electrical and mechanical properties. However, unlike other graphene-containing networks, the specific surface area of the cast tapes remains high (>400 $m^2 \cdot g^{-1}$). Exhibiting apparent densities between 0.15 and 0.51 $g^3 \cdot cm^{-3}$, with electrical conductivities up to 24 $kS \cdot m^{-1}$ and tensile strengths over 10 MPa, these tapes exhibit the best combination of properties with respect to density heretofore observed for carbon-based papers, membranes, or films.[15]

Controlling the Size of Graphene Oxide Sheets

We have studied the effect of the oxidation path and the mechanical energy input on the size of graphene oxide sheets derived from graphite oxide. The cross-planar oxidation of graphite from the (0002) plane results in periodic cracking of the uppermost graphene oxide layer, limiting its lateral dimension to less than 30 μm. We used an energy balance between the elastic strain energy associated with the undulation of graphene oxide sheets at the hydroxyl and epoxy sites, the crack formation energy, and the interaction energy between graphene layers to determine the cell size of the cracks. As the effective crack propagation rate in the cross-planar direction is an order of magnitude smaller than the edge-to-center oxidation rate, graphene oxide single sheets larger than those defined by the periodic cracking cell size are produced depending on the aspect ratio of the graphite particles. We also demonstrated that external energy input from hydrodynamic drag created by fluid

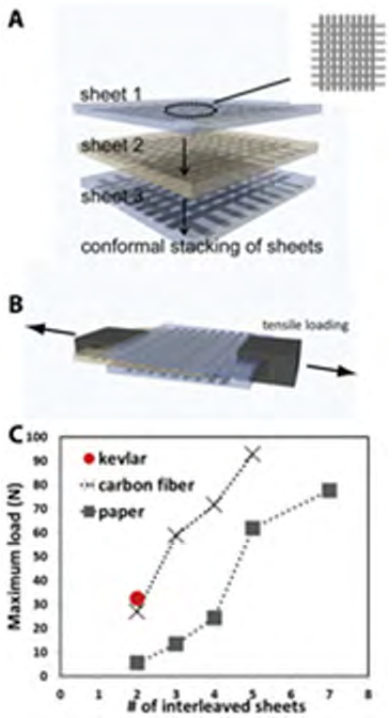

Figure 20. (a) Schematic of stacked, fiber reinforced elastomeric sheets. (b) Schematic of tensile load test. (c) Tensile load trends as a function of interleaved sheet number.

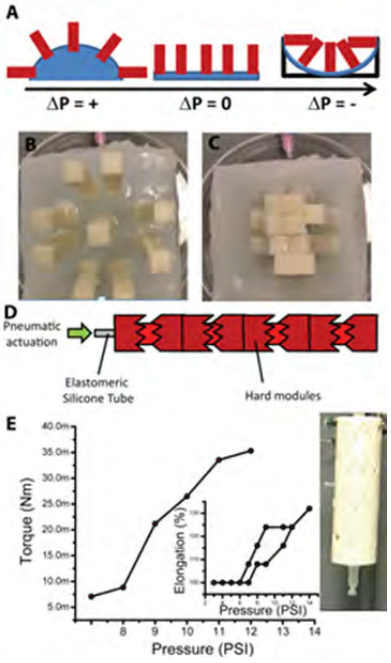

Figure 21. (a) Schematic operation of the a 2D jamming surface. (b) Photograph of a test structure unjammed and (c) jammed. (d) Schematic of a 1D jamming surface. (e) Torque and elongation plots. Inset is a photograph of the device jammed.

motion or sonication, further reduces the size of the graphene oxide sheets through tensile stress buildup in the sheets.[16]

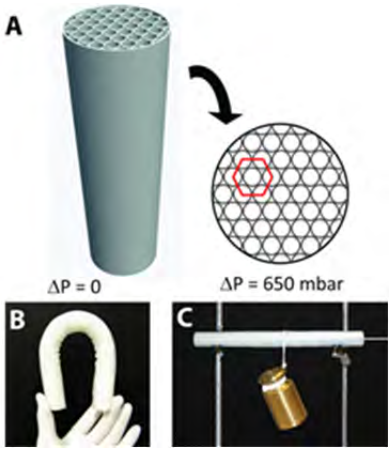

Figure 22. (a) Schematic of the pneumatic bone architecture. Each circle represents an inflatable tube. (b) The bone is flexible when not pressurized but stiff (c) when pressurized.

FGS in Dye-Sensitized Solar Cells

Several techniques for fabricating FGS electrodes were tested for catalytic performance in dye-sensitized solar cells (DSSCs). By using ethyl cellulose as a sacrificial binder, and partially thermolyzing it, we were able to create electrodes which exhibited lower effective charge transfer resistance (<1 $\Omega \cdot cm^2$) than the thermally decomposed chloroplatinic acid electrodes traditionally used. This performance was achieved not only for the triiodide/iodide redox couple, but also for the two other major redox mediators used in DSSCs, based on cobalt and sulfur complexes, showing the versatility of the electrode. DSSCs using these FGS electrodes had efficiencies (η) equal to or higher than those using thermally decomposed chloroplatinic acid electrodes in each of the three major redox mediators: I (η_{FGS} = 6.8%, η_{Pt} = 6.8%), Co (4.5%, 4.4%), S (3.5%, 2.0%). Through an analysis of the thermolysis of the binder and composite material, we determined that the high surface area of an electrode, as determined by nitrogen adsorption, is consistent with but not sufficient for high performing electrodes. Two other important considerations are that (i) enough residue remains in the composite to maintain structural stability and prevent restacking of FGSs upon the introduction of the solvent, and (ii) this residue must not disperse in the electrolyte.[17]

FGS in Batteries

The lithium-air battery is one of the most promising technologies among various electrochemical energy storage systems. We demonstrate that a novel air electrode consisting of an unusual hierarchical arrangement of functionalized graphene sheets (with no catalyst) delivers an exceptionally high capacity of 15,000 mAh/g in lithium-O_2 batteries which is the highest value ever reported in this field. This excellent performance is attributed to the unique bimodal porous structure of the electrode which consists of microporous channels facilitating rapid O_2 diffusion while the highly connected nanoscale pores provide a high density of reactive sites for LiO_2 reactions. Further, we show that the defects and functional groups on graphene favor the formation of isolated nanosized Li_2O_2 particles and help prevent air blocking in the air electrode. The hierarchically ordered porous structure in bulk graphene enables its practical applications by promoting accessibility to most graphene sheets in this structure.[18]

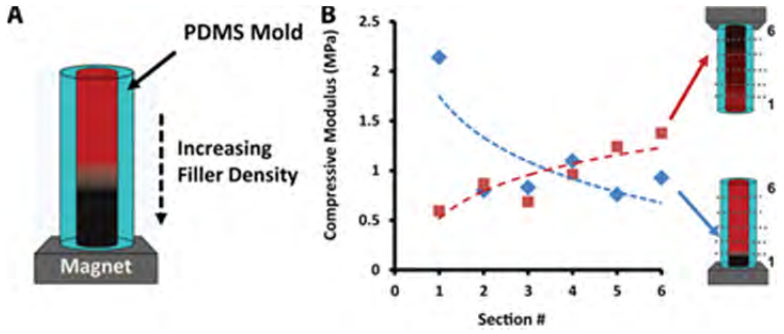

Figure 23. (a) Schematic showing creation of the graded structure. Uniform heating is applied and the filler is pulled toward the magnet. (b) We can create gradients with and against the force of gravity. By sectioning the resulting structures and measuring their compressive moduli we see the expected trend: the stiffest sections are toward to magnet.

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TECHNOLOGY TRANSFER

None during report period

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Lidiya Mishchenko (Ph.D.), Harvard University (Aizenberg)
Shuyang Pan (Ph.D.), Princeton University (Aksay)
Lauren Zarzar (Ph.D.), Harvard University (Aizenberg)

UNDERGRADUATE STUDENT METRICS

All items refer to graduating undergraduates funded by this agreement and the reporting period for this report.

Number of graduating undergraduate students:	10
Number of undergraduate students graduating with degrees in science, mathematics, engineering, and technology fields:	10
Number of graduating undergraduates who will continue to pursue graduate degrees:	5
Number of graduating undergraduates who intend to work for the Defense Department:	1
Number of graduating undergraduates during this period who achieve a 3.5 to 4.0 GPA (Convert GPAs on any other scale to be an equivalent value on a 4.0 scale.):	9
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields.:	2

FORECAST EXPENDITURES

SECTION 2: ACCOUNTING AND FORECASTING OF EXPENDITURES - Completed by PI

1. Expenditures (cost incurrence's from date of contract/grant as of date of receipt of this request or as of most recent cut-off in accounting records: $ 3,750,000 (5/31/2013)
2. Additional projected expenditures before 01-Jun-2014: $0
3. Forecast expenditures for the proposed period of extension: Not applicable

* The projected total funding (sum of lines 1, 2 and 3) cannot exceed the sum of the current and planned extension funding identified in SECTION 1. If the forecast expenditures differ significantly from the budget previously negotiated and included in the research agreement, a new budget must be submitted. A “significantly different” budget is defined as: (i) a decrease in the planned funding level cited above or (ii) a deviation of 10% (plus or minus) to any cost element (direct labor, indirect expense, travel, etc.) included in the budget.